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14. ABSTRACT

The syntheses and characterization of five groups of energetic salts: 5-nitroiminotetrazolates, mono-oxy-nitroiminotetrazolates and bis-oxy-nitroiminotetrazolates; 1-hydrazinyl-2,2-dinitro-ethanamine salts; 5-nitro-3-trinitromethyl-1H-1,2,4-triazolates, and 5,5'-bis (trinitromethyl)-3,3'-azo-1H-1,2,4-triazolates; 3,4,5-trinitropyrazolate; and trinitropyrazole-1-olate salts; and three groups of energetic molecular compounds: polynitramines, mono-, di-, and trisubstituted nitroiminotetrazoles, and trinitromethyl-substituted 5-nitro or 3-azo-1,2,4-triazoles are described. The presence of nitro group(s) contributes markedly to the oxygen content in our effort to synthesize materials to compete successfully with ammonium perchlorate as the oxidizer of choice. Many of these materials have properties, including more positive heats of formation (kJ/g), competitive detonation pressures and velocities, and lower impact sensitivities, superior to those of RDX and, in some cases, of HMX. Very often water is the reaction solvent of choice which speaks positively to hydrolytic stability and enhances the greenness of the synthesis.

15. SUBJECT TERMS

nitro, energetic salts, energetic molecular compounds, polynitramines, nitroiminotetrazoles, trinitromethyl-substituted 1,2,4-triazoles, 3,4,5-trinitropyrazolate, trinitropyrazole-1-olate, mono-oxy and bis-oxy-nitroiminotetrazolates, 1-hydrazinyl-2,2-dinitro-ethanamine salts

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Nitroamino and Nitro Energetics
Final Technical Report (09-13-2012)
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Introduction

An overview of a few of the new most energetic salts and molecular species as measured by the magnitudes of heats of formation and detonation properties, oxygen content, and impact sensitivities synthesized at the University of Idaho with ONR support during FY 2010-2012 (Nitroamino and Nitro Energetics - N00014-10-0097) is presented in this report

The development of an accurate empirical method for estimation of densities of salts and molecular compounds is a major contribution to an area where prior knowledge is particularly useful to guide the synthetic hand. The trinitromethanide anion introduces excellent explosive and propellant properties into salts with azolium cations. While many of these salts have appreciable positive enthalpies and densities, they tend to have low thermal stabilities ($T_d \leq 120$ °C). The 2,4,5-trinitroimidazolates possess relatively high densities (>1.75 g cm^{-1}) and thermal stabilities ($T_d > 198$ °C) with detonation pressures and velocities comparable to those of explosives, such as TATB and RDX. Properties of energetic mono- and di-basic 5-dinitromethyltetrazolate salts with a variety of high nitrogen cations compete with explosives such as TNT, NTO, TNAZ, and ADN. Synthesis of nitroiminotetrazolate salts provides a new and straightforward approach to highly energetic salts where all of the new salts exhibit good physical properties, such as good thermal and hydrolytic stabilities, high densities, and useful heats of formation. These compounds show calculated detonation pressures and velocities comparable to those of explosives such as HMX. Energetic molecular compounds – polynitramines, mono-, di-, and trisubstituted nitroiminotetrazolazoles, and trinitromethyl-substituted 5-nitro or 3-azo-1,2,4-triazoles – occasionally compete successfully with ammonium perchlorate as the oxidizer of choice. Many of these molecular materials have properties, including more positive heats of formation (kJ/g), competitive detonation pressures and velocities, and lower impact sensitivities, superior to those of RDX and, in some cases, of HMX. Very often water is the reaction solvent used which speaks positively to hydrolytic stability and enhances the greenness of the synthesis. See Appendix for the most highly energetic materials.

Results and Discussion

This report describes the synthesis and characterization of five groups of energetic salts: 5-nitroiminotetrazolates, mono-oxy-nitroiminotetrazolates and bis-oxy-nitroiminotetrazolates; 1-hydrazinyl-2,2-dinitro-ethanamine salts; 5-nitro-3-trinitromethyl-1H-1,2,4-triazolates, and 5,5'-bis(trinitromethyl)-3,3'-azo-1H-1,2,4-triazolates; 3,4,5-trinitropyrazolate; and trinitropyrazole-1-olate salts; and three groups of energetic molecular compounds: polynitramines, mono-, di-, and trisubstituted nitroiminotetrazoles, and trinitromethyl-substituted 5-nitro or 3-azo-1,2,4-triazoles. The presence of nitro group(s) contributes markedly to the oxygen content in our effort to synthesize materials to compete successfully with ammonium perchlorate as the oxidizer of choice. Many of these materials have properties, including more positive heats of formation (kJ/g), competitive detonation pressures and velocities, and lower impact sensitivities, superior to those of RDX and, in some cases, of HMX. Very often water is the reaction solvent of choice which speaks positively to hydrolytic stability and enhances the greenness of the synthesis.

A. Polynitramines[1g]

Various energetic compounds have been investigated as precursors of high density energetic nitrimino,[1] nitramino,[2] nitro,[3] or nitrato[1a,3c,d] compounds. In particular, high-energy polyazapolycyclic caged polynitramines have emerged as a promising family of high energy density materials.[2a] The current well known polynitramino compounds are RDX, HMX and CL-20.

Primary nitramine molecules [dinitrourea (DNU),[4] methylene dinitramine (MDNA)[5] and ethylene dinitramine (EDNA)[6]] have impressive high densities, positive oxygen balances (except EDNA) and good detonation properties. However, the application of primary nitramines as energetic materials is limited due to their relatively low thermal stability (for DNU[4c]: T_{dec}: 92 °C, for MDNA[5]: T_{dec}: 98–101 °C). Thermal decomposition studies involving aliphatic primary nitramines have led to an understanding of the relationship between structure and thermostability, and to the suggestion of a decomposition mechanism for these compounds.[7a,b] Increasing the number of nitro groups in a molecule in order to obtain a more balanced and powerful explosive inevitably results in an increase in acidity and a decrease in thermal stability of the resulting compounds.[7]

The synthesis of a new energetic pentaerythrityl tetranitramine (PETNA) 4 that exists as colorless crystals at ambient temperature, thermally decomposes at 183 °C, and has high density, was successful. Also described are the chemical, thermal, and sensitivity properties of 4, as well as some preliminary calculated detonation properties (Scheme 1).
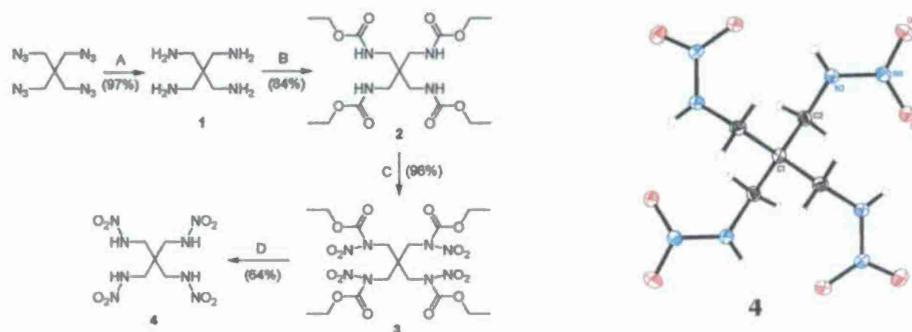

Scheme 1. Synthesis of pentaerythrityl tetranitramine (PETNA) 4; A: H_2/Pd/C, B: ClCOOCH$_2$CH$_3$, C: 100% HNO$_3$/(CF$_3$CO)$_2$O, D: 28% aq.

Other successful syntheses of polynitramines 5 (77%), which was proved by single crystal x-ray diffraction analysis, 6 (79%) and 7 (90%) by analogous nitration of polyurethane derivatives with concomitant retention of the pentaerythritol system resulted from extension of this reaction (Scheme 2).
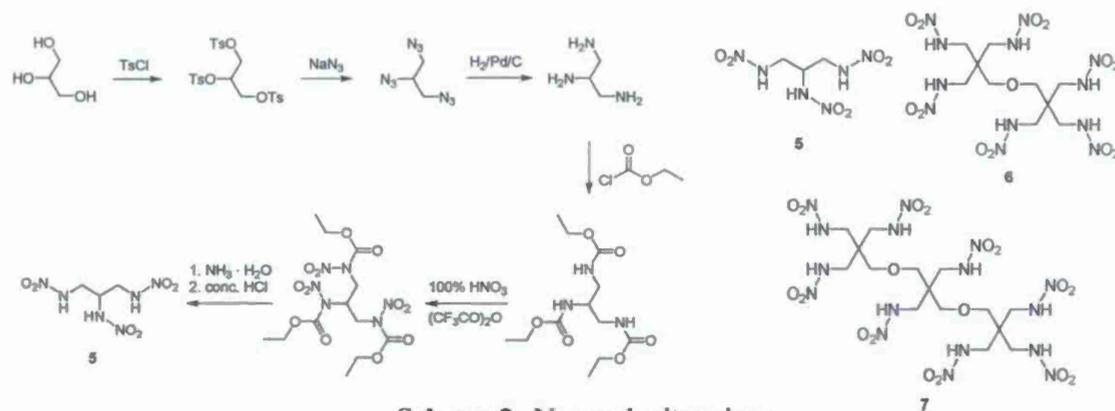
Scheme 2. New polynitramines.

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The preparation of an asymmetric tetranitramine **11** was attempted by analogous nitration of the asymmetric tetraurethane **8** (Scheme 3). When the latter was nitrated with 100% nitric acid in trifluoroacetic anhydride, only a trinitro-substituted carbamate **9** was obtained as a colorless oil in a yield of 96%. Incomplete substitution of nitro groups results from steric hindrance of the three nitro urethane groups; this is significantly different from methylene bridged nitro urethane **3**. The reaction of the asymmetric nitramine **10** with excess hydrazine hydrate in ethanol provided a further approach to the trihydrazinium salt.
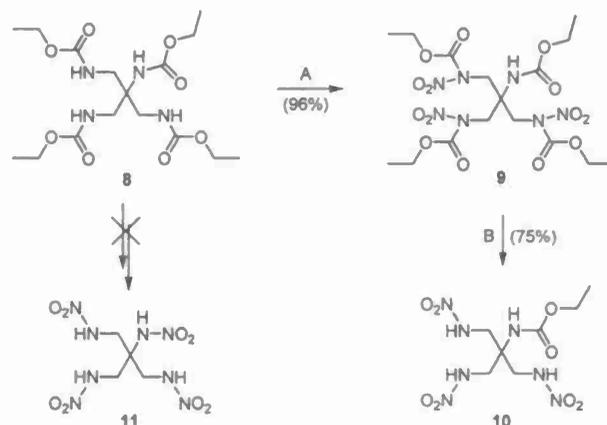
Scheme 3. Attempt to synthesize asymmetric tetranitramine **11**; A: 100% HNO$_3$/(CF$_3$CO)$_2$O, B: 28% aq. NH$_3$/36% HCl.

The ^{15}N NMR spectra[8] of the polynitramines measured in [D$_6$]DMSO show two or four resonances for nitrogen of NO$_2$ and NH. In the spectra, a typical chemical shift for NO$_2$ is observed between −23.1 and −17.8 ppm. The nitrogen signals from NH are found between −207.6 and −195.7 ppm at higher field than the starting material of polynitrourethane (between −167.8 and −173.0 ppm) and lower field than polyurethane with respect to the electronegativity effect.

The thermal behavior of **4−7**, which have decomposition temperatures between 181 and 185 °C (PETN: 160 °C, NG: 50−60 °C), was investigated using differential scanning calorimetry (Table 1). Only tris(nitramino)propane (**5**) shows a melting point (133 °C). Calculation of the heats of formation for polynitramines **4** and **5** was accomplished by using the Gaussian 03 suite of programs.[9] The geometric optimizations of the structures and frequency analyses were carried out by using the B3LYP functional with the 6−31+G** basis set, and zero-point energies were calculated at the MP2/6−311++G** level (Table 1).

All of the polynitramines exhibit negative heats of formation with **4** and **5** having the least negative −0.193 and 1.450 kJ g^{-1} (PETN: −1.590 kJ g^{-1}, NG: −1.548 kJ g^{-1}). The detonation parameters [pressures (P) and velocities (D)] were calculated using the CHEETAH 5.0 computer program. For **4** and **5** the calculated detonation pressures are 31.59 and 35.62 GPa (PETN: 31.39 GPa, NG: 25.3 GPa). Detonation velocities are 8657 and 8933 m s^{-1}, respectively (PETN: 8564 ms^{-1}, NG: 7700 m s^{-1}). The impact sensitivity was tested according to BAM methods (BAM Fallhammer). In Table 1, there is a range in impact sensitivities from the sensitive **4** (6 J) to **5** (20 J) and finally to the insensitive compound **6** (> 40 J) and **7** (> 40 J). The sensitivity of these polynitramino compounds is greatly reduced compared to PETN (2.9 J) and NG (0.2 J).

Table 1. Physical properties of polynitramines **4** and **5** compared with PETN, NG and RDX*

compd	$T_d{}^a$ [°C]	density^b [g cm^{-3}]	$\Delta_f H^o{}_{298}{}^c$ [KJ g^{-1}]	P^d [GPa]	D^e [m s^{-1}]	IS^f J	OP^g [%]
4	183	1.778	−0.193	31.6	8657	6	41
5	183^h	1.753^i	1.450	35.6	8933	20	43
PETN^j	160	1.778	−1.590	31.4	8564	2.9	61
NG^k	50−60	1.60	−1.548	25.3	7700	0.2	63
RDX^j	230	1.816	0.42	35.2	8977	7.4	43

*Syntheses of all compounds are given in Reference 1g. ^{a} Thermal decomposition temperature under nitrogen gas (DSC, 10 °C min^{-1}). ^{b} Gas pycnometer (25 °C). ^{c} Heat of formation (using 83.68 kJ mol^{-1} for the enthalpy of sublimation for each compound; calculated via Gaussian 03). ^{d} Calculated detonation pressure (CHEETAH 5.0). ^{e} Calculated detonation velocity (CHEETAH 5.0). ^{f} Impact sensitivity (BAM Fallhammer). ^{g} OP = Oxygen percentage. ^{h} **5** melts at 133 °C. ^{i} Determined by X-ray crystallography (20 °C). ^{j} PETN = pentaerythrityl tetranitrate, RDX = 1,2,5-trintrinitro-1,3,5-triazacyclohexane. ^{k} NG = nitroglycerine.

B. Mono- or bis-oxy 5-nitroiminotetrazole derivatives[10b]

This work led to a series of nitroiminotetrazole derivatives of oxy nitroiminotetrazoles and their salts, with potentially significant physical and energetic properties. The aim of our study was to elucidate the structures in the crystalline state using x-ray diffraction analysis and to find new, potent oxygen and nitrogen rich tetrazoles. Alkoxy 5-nitroiminotetrazolates may be of interest as a new class of ionic energetic materials, which have good thermal stabilities, high densities, good oxygen balance, and high heats of formation and which are realizable in high yields via straightforward routes. The synthesis of 1-methoxy-5-aminotetrazole (**13**) was achieved from the reaction of cyanogen azide with methoxy amine (Scheme 4). At ambient temperature, nitration of aminotetrazole, **13**, using 100% nitric acid without solvent formed 1-methoxy-5-nitroiminotetrazole, **14**, in good yield. The new energetic salts **15** and **16** were easily obtained by reacting **14** with a slight excess of 28% aqueous ammonia or 97% hydrazine hydrate in water, respectively. The structures of methoxy nitroiminotetrazole and its salts are supported by IR, and ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic data as well as elemental analysis. Structural confirmation of **14** by single crystal x-ray diffraction analyses is given in Figure 1a.

Methylene bridged nitroiminotetrazoles are particularly exciting molecules as high energy density materials. We were interested in utilizing our well-established 5-aminotetrazole synthesis methodology with the highly sterically hindered diaminomethane. Unfortunately, addition of the methylene diamine to cyanogens azide failed. However it was possible to prepare
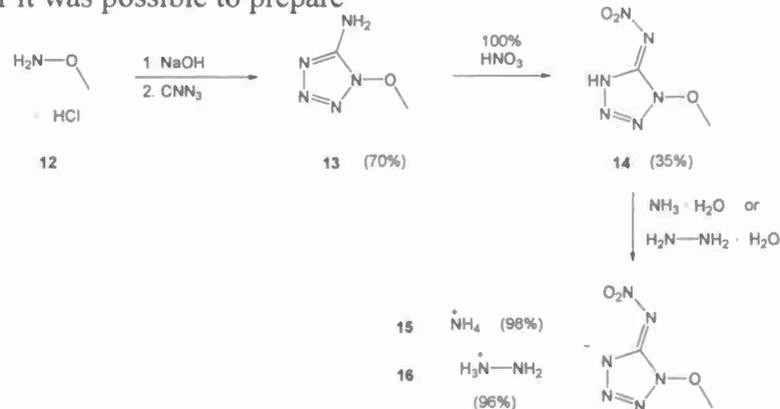
**Scheme 4.** Synthesis of **14** and its salts.

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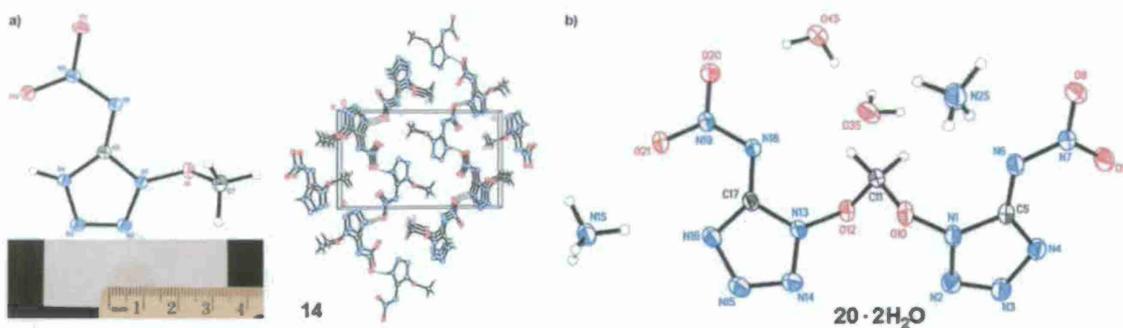
Figure 1. Crystal structures of **14** and **20**.

18 by the analogous reaction of cyanogen azide with the less sterically hindered methylene bis(oxyamine) (Scheme 5), and to investigate energetic ionic liquids based on this bisoxyamine. Nitration of **18** with 100% nitric acid led to the extremely sensitive **19**.
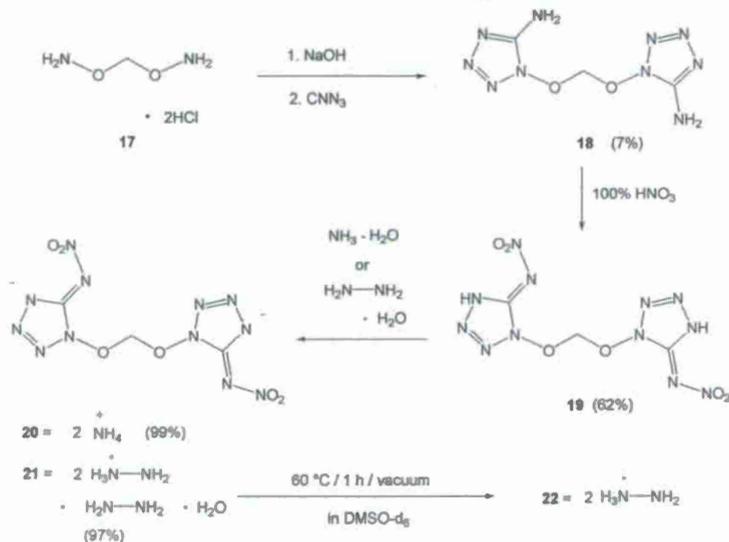

Scheme 5. Synthesis of **19** and its salts.

The structures of **17**, **18**, and **19** are supported by IR, and ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic data as well as elemental analysis. Structural confirmation of **20**·2H$_2$O by single crystal x-ray diffraction analyses is given in Figure 1b. Compounds **17** and **18** decomposed slowly in DMSO[D$_6$] during NMR measurements. While elemental analyses were successfully carried out for salts **20** and **21**, an attempted elemental analysis for neutral **19** resulted in a violent detonation in the apparatus during the measurement. Although attempts to remove the hydrazine and water molecules in the crystal of **21** to give **22** at 60 °C under high vacuum were unsuccessful, it was possible to remove these species under the same conditions from a solution in DMSO[D$_6$].

Next similar successful attempts were made to prepare **24** and **25** in good yield. The energetic salts **26** and **27** were generally obtained by acid-base reactions with **25**·3H$_2$O and energetic bases (Scheme 6). Attempted elemental analyses for neutral alkoxy-5-nitroimino-tetrazoles **25**·3H$_2$O and **25** resulted in violent detonations in the apparatus during measurement.

As expected and found in several structures of oxy 5-nitroiminotetrazoles and their salts discussed in this work, the five membered ring is nearly planar, building an aromatic system, which can be seen by the torsion angle N1−N2−N3−N4 of between 0.09(10)° and
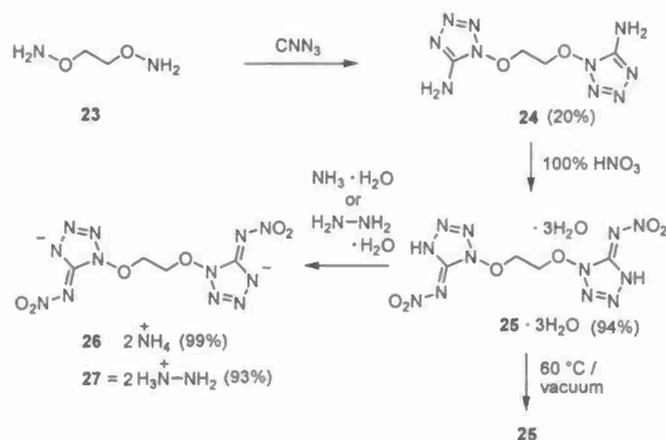
Scheme 6. Synthesis of **25** and its salts.

0.10(17)°. The ring moieties of **14** and **20**·2H$_2$O (Figure 1a and b) are in agreement with the geometry observed for 5-nitroiminotetrazoles and their salts.

Heat of formation is one of the important characteristics for energetic salts which is directly related to the number of nitrogen-nitrogen bonds in an ionic species. All *ab initio* calculations were carried out using the program package Gaussian 03 (Revision D.01).[9] The geometric optimization of the structures and frequency analyses was accomplished by using the B3LYP with the 6-31+G** basis set, and single-point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated by the G2 method. In Table 2 it is shown that all alkoxy nitroiminotetrazoles and their salts are highly endothermic compounds. The enthalpies of energetic materials are controlled by the molecular structure of the compounds. Consequently, heterocycles with higher nitrogen content, especially tetrazole, show higher heats of formation. All of the compounds exhibit positive heats of formation with **19** having the highest value at 3.58 kJ g^{-1} and **26** which in spite of the lower nitrogen content has a high positive heat of formation with a value at 2.24 kJ g^{-1}.

By using the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer values, 25 °C) of the new highly energetic oxy-nitroiminotetrazoles, and their salts, the detonation pressures (P) and detonation velocities (D) were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using Cheetah 5.0 (Table 2).[14] The calculated detonation pressures of oxy nitroiminotetrazoles and their

Table 2. Physical properties of oxy nitroiminotetrazoles, and their salts compared with RDX and HMX.*

compd	T_{dec}[a] [°C]	d[b] [g cm^{-3}]	ΔH_f°[c] [kJ g^{-1}]	P[d] [GPa]	D[e] [m s^{-1}]	IS[f] [J]	O[g] [%]
14	116	1.66	3.15[h]	31.5	8660	5	30
15	184	1.55	2.40	27.7	8448	1.5	27
16	156	1.63	2.98	32.3	9036	4	25
19	157	1.90	3.58[h]	46.7	9867	1	32
20	167	1.71	2.38	33.9	8984	1	28
25	134	1.81	3.47[h]	38.4	9200	1.5	30
26	202	1.72	2.24	33.3	9014	2	27
27	169	1.73	2.92	35.5	9305	1.5	25
RDX	230	1.82	0.42	35.2	8977	7.4	43
HMX	287	1.91	0.35	39.6	9320	7.4	43

* Syntheses of all compounds are given in Reference 10b. [a] Thermal decomposition temperature under nitrogen gas (DSC, 5 °C min^{-1}); No melting points are observed. [b] From gas pycnometer (25 °C). [c] Heat of formation (calculated via Gaussian 03). [d] Calculated detonation pressure

(Cheetah 5.0). [e] Calculated detonation velocity (Cheetah 5.0). [f] Impact sensitivity (BAM drophammer). [g] O = Oxygen percentage. [h] Solid state.

salts lie in the range between $P = 27.7$ and $P = 46.7$ GPa (comparable to RDX = 35.2 GPa and HMX = 39.6 GPa). Detonation velocities lie between $D = 8448$ and $D = 9867$ m s^{-1} (comparable to RDX = 8977, HMX = 9320 m s^{-1}). These properties coupled with the rather high thermal and hydrolytic stabilities make these high-nitrogen materials attractive candidates for energetic applications. The relatively good oxygen balances of **19**, **20**, and **25** are −11%, −24%, and −25%, respectively, which are comparable with those of RDX (−22%) and HMX (−22%).

In summary, compounds **19**, **25**, and **27** exhibit good physical and detonation properties, such as moderate thermal stabilities, high densities, highly endothermic, good detonation properties. Calculated detonation values of these compounds are comparable to those of explosives such as HMX ($P = 39.63$ GPa, $D = 9320$ m s^{-1}). However, they are very impact sensitive falling between 1 and 1.5 J. The impact sensitivity of these compounds could be reduced by combination with a less sensitive oxidizer, e. g., ammonium nitrate.

C. Nitroimino-tetrazolates and oxy-nitroimino-tetrazolates – a comparison[10a]

One high nitrogen system extensively studied by the Idaho group is the substituted nitroiminotetrazole. By employing an alternate route, we reported the effective synthesis of the di-substituted 5-nitroiminotetrazoles, 1,1'-ethylenebis(5-nitroiminotetrazole) (**28**)[1a] and 1,1'-ethylenebis(oxy)bis(5-nitroiminotetrazole) (**29**)[10] (Figure 2). The development of disubstituted 5-
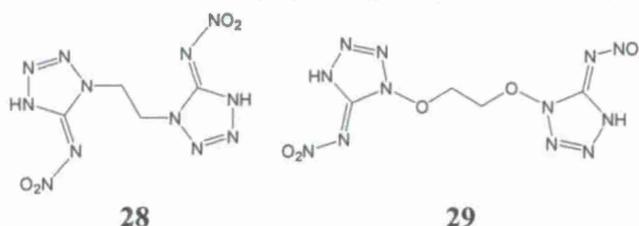

**Figure 2.** Bis(5-nitroiminotetrazole) **28** and **29**.

aminotetrazole compounds was extended by the utilization of an excellent in situ method which involved reactions of cyanogen azide[11] and primary amines. Nitration of these aminotetrazoles using 100% nitric acid has been shown to form di-substituted nitroiminotetrazole derivatives. Compound **28** exhibits a high measured density of 1.858 g cm^{-3}; calculated heat of formation of 3.63 kJ g^{-1}; detonation pressure of 38.19 GPa; and a detonation velocity of 9329 m s^{-1}. The values of the detonation properties of compound **29** ($P = 38.38$ GPa, $D = 9200$ m s^{-1}) are as high as for compound **28** and its oxygen percentage is slightly improved. Impact sensitivity measurements on oxy nitroiminotetazole **29** indicate that it is very sensitive to shock; accordingly it should be handled with caution and in small amounts. For this reason, **29** needs to be desensitized perhaps by salt formation. Recently we reported that reduced sensitivity was obtained by making energetic salts of compound **28** and energetic bases.[1b] The formation of salts of the nitroiminotetrazole led to an enhanced thermal stability and less or equal impact sensitivity compared to neutral compound.

The aim of this work was to prove the structures of important crystalline energetic salts using X-ray diffraction analysis and to discover new and potent nitroiminotetrazolate salts. Oxy 5-nitroiminotetrazolate salts are of interest as ionic energetic materials, which have good thermal stabilities and low impact sensitivities, and which deserve closer attention by researchers because they are closely linked with the safety of handling and application of explosives. Here, we compare properties of the new oxy nitroiminotetrazolate salts with new as well as our previously reported nitroiminotetrazolate salts.[1b]

A convenient method for the synthesis of 1,1'-ethylenebis(oxy)bis(5-aminotetrazole) **24** from **23** and cyanogen azide without the intermediate isolation of imindoylazide was developed

and resulted in the preparation of the target oxy aminotetrazole **24** in 20% yield. The corresponding high energetic oxy nitroiminotetrazole **29** was prepared from oxy aminotetrazole **24** in good yield by a nitration procedure from the literature.[10] Attempts to remove water molecules in the crystal of **29·2H₂O** to give **29** at 60 °C under high vacuum were successful. Violent detonations during attempted elemental analyses determinations, compound **29** and **29·2H₂O** were not analyzed.

Fortunately, it was possible to perform single crystal x-ray diffraction analysis for **33·2H₂O** (Figure 3). The energetic salts **31−34** were generally obtained by acid-base reactions between **29** and energetic bases in aqueous solutions (Scheme 7). Also, in Scheme 7 is shown the syntheses of the diaminoguanidinium and triaminoguanidinium oxy nitroiminotetrazolate salts. Two energetic salts, **35** and **36,** were synthesized using silver 1,1'-ethylenebis(oxy)bis(5-nitroiminotetrazolate) (**30**), which was obtained by metathesis of sodium 1,1'-ethylenebis(oxy)bis(5-nitroiminotetrazolate) and silver nitrate, with the corresponding chloride
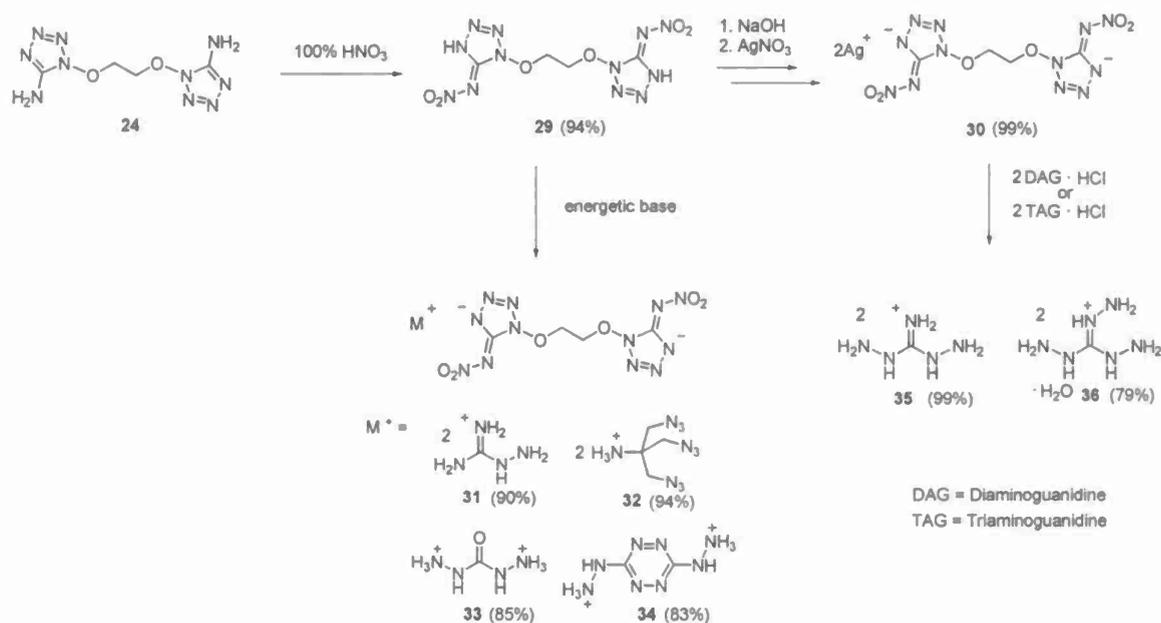
Scheme 7. Synthesis of 1,1'-ethylenebis(oxy)bis(5-nitroiminotetrazolate) salts.

salts. After stirring for four hours, silver chloride from the suspension was filtered and the filtrate was dried. The structures of 1,1'-ethylenebis(oxy)bis(5-nitroiminotetrazole) (**29**) and its salts are supported by IR, and ¹H, ¹³C, and ¹⁵N NMR spectroscopic data as well as elemental analysis.

Next similar successful attempts were made to prepare bis(diaminoguanidinium) 1,1'-ethylenebis(5-nitroiminotetrazolate) (**38**) and bis(triaminoguanidinium) 1,1'-ethylenebis(5-nitroiminotetrazolate) (**39**) in good yields by metathesis with silver salt **37** (Scheme 8). The structures of **38** and **39** are supported by IR, and ¹H, ¹³C, and ¹⁵N NMR spectroscopic data as well as elemental analysis. Salt **39** also could be prepared by metathesis reactions of barium 1,1'-ethylenebis(oxy)bis(5-aminotetrazolate) with the corresponding triaminoguanidinium sulfate in a yield of 74%.

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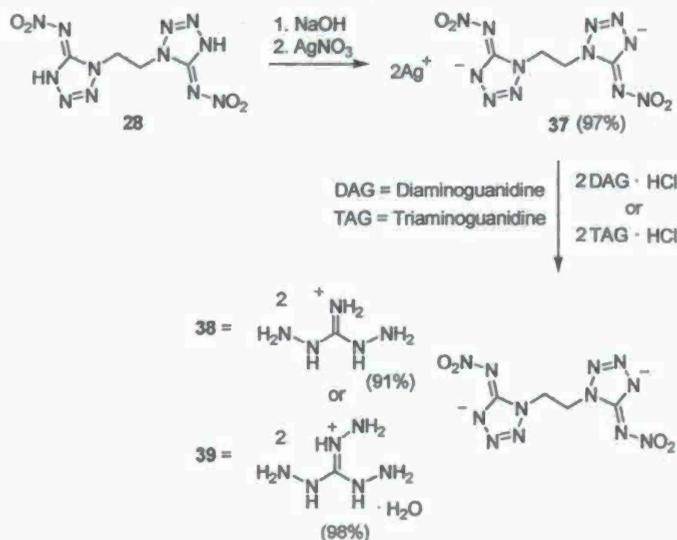
Scheme 8. Synthesis of 1,1'-ethylenebis(5-nitroiminotetrazolate) salts by metathesis.

Compound **33**·2H$_2$O crystallized in a triclinic cell in the space group P-1 with two molecules in the unit cell. The tetrazole ring of **33**·2H$_2$O is nearly planar and four similar bond lengths are observed [N1–N2 = 1.336(16) Å, N3–N4 = 1.369(19) Å, N4–C5 = 1.326(16) Å, N1–C5 = 1.349(18) Å], and shows the delocalization of the negative charge from the ring (Figure 3). The main change observed is the bond length of N2–N3 which corresponds to the N4 nitrogen atom that undergoes deprotonation in **28**. Deprotonation results in a lengthening of the N1–N2 and N3–N4 distances (ca. 0.01 Å) and a shortening of the N2–N3 bond (ca. 0.02 Å). These distances are considerably longer than N2–N3 double bonds (1.291(2) Å) but significantly shorter than the O10–C11 [1.461(17) Å] or N1–O10 [1.363(14) Å] single bond. The nitroimine unit lies in the plane of the tetrazole ring as clearly shown by the C5–N6–N7–O9 torsion angle of −0.57(18)° and C5–N6–N7–O8 torsion angle of −179.27(11)°, in which the oxygen atoms O8 and O9 are twisted slightly out of the plane. The ethoxy unit does not lie in the plane of the tetrazole ring [torsion angle C5–N1–O10–C11 of 91.50(15)°]. The observed angle in the tetrazolate matches the typical values found in the literature for oxy nitroiminotetrazolate.[10]
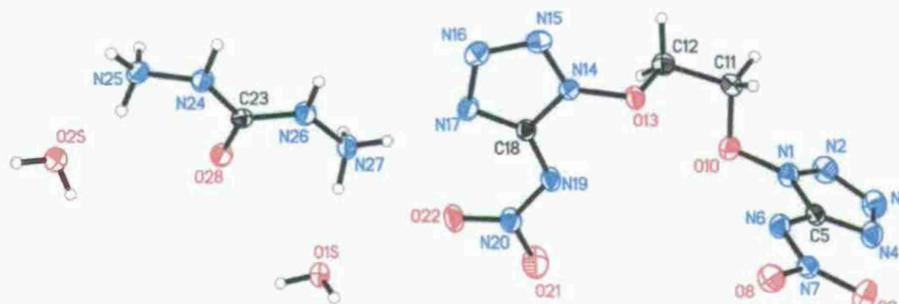
Figure 3. A view of the molecular unit of **33**·2H$_2$O. Thermal ellipsoids represent 50% probability.

In Table 3 it is shown that all nitroiminotetrazolate salts are highly endothermic compounds. The enthalpies of energetic materials are controlled by the molecular structure of the compounds. Consequently, heterocycles with higher nitrogen content, especially tetrazole, show higher heats of formation. All of the new compounds (**31–36**, **38** and **39**) exhibit positive heats of formation ranging between 2.21 and 4.14 kJ g^{-1}. Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium] 1,1'-ethylenebis(oxy)bis(5-nitroiminotetrazolate) (**32**) has the highest value at 4.14 kJ g^{-1} which is comparable to salt (**TAA I-8**)[14] of the same cation and anion **28**$^{2-}$ with a high positive heat of formation (4.31 kJ g^{-1}). Impact sensitivity measurements were made using standard BAM Fallhammer techniques.[13] Listed in Table 3 are impact sensitivities ranging from

those of the relatively less sensitive **31**, **33**, **33·4H₂O**, **34·2H₂O**, **35**, **36**, and **38**, between 4 J and 8 J to the very sensitive compounds **32**, **33·2H₂O**, and **34** between 1 J and 2 J. Compounds **38·2H₂O** and **39** are not impact sensitive. Thermal stabilities of the energetic compounds were studied with differential scanning calorimetry (DSC) at a scan rate of 10 °C min^{-1}. All nitroiminotetrazolates decomposed between 130 and 220 °C. As expected the thermal stabilities for all energetic salts are higher for the neutral compounds **28** (194 °C) and **29** (125 °C). The most thermally stable derivatives of **29** and **28** are the aminoguanidinium salts **31** and **AG I-8** where decomposition occurred at 200 and 255 °C, respectively (Table 3). By using the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer or X-ray values) of the new highly energetic nitroiminotetrazolate salts, **31–36**, **38**, and **39**, the detonation pressures (P) and detonation velocities (D) were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using Cheetah 5.0 (Table 3).[14] The calculated detonation pressures of nitroiminotetrazolate salts lie in the range between $P = 26.51$ and $P = 33.25$ GPa (comparable to TATB = 31.15, RDX = 35.17 GPa). Detonation velocities lie between $D = 8377$ and $D = 9030$ m s^{-1} (comparable to TATB = 8114, RDX = 8977 m s^{-1}). These

Table 3. Physical properties of oxy nitroiminotetrazolate salts **31-36** compared with nitroiminotetrazolate salts **38-39**.*

compd	T_m[a] [°C]	$T_{dec.}$[b] [°C]	Density[c] [g cm^{-3}]	ΔH_f°[d] [kJ mol^{-1} (kJ g^{-1})]	P[e] [GPa]	D[f] [m s^{-1}]	IS[g] [J]	OB[h] [%]
31	–	200	1.602	1029 (2.21)	26.78	8472	6	−51
32	–	151	1.597	2944 (4.14)	26.56	8377	< 1	−63
33	–	130	1.695	1134 (2.78)	32.20	8789	6	−35
33·2H₂O	127	156	1.716[i]	–	–	–	2	−35
33·4H₂O	71, 78, 129	147	1.647	–	–	–	8	−35
34	–	147	1.780	1270 (2.76)	33.25	9030	2	−42
34·2H₂O	72	131	1.683	–	–	–		−42
35	160	164	1.675[i]	1254 (2.53)	28.72	8741	5	−52
36	95, 160	162	1.607	1487 (2.82)	29.36	8840	4	−52
38	–	220	1.577	1233 (2.66)	26.51	8568	7	−62
38·2H₂O	202	218	1.639[i]	–	–	–	> 40	−62
39	132	195	1.601	1458 (2.95)	28.64	8860	> 40	−61
AG I-8[j]	–	255	1.610	993 (2.29)	26.27	8531	10	−63
TAA I-8[k]	–	186	1.600	2922 (4.31)	26.45	8429	5	−73
CH I-8[l]	–	203	1.722	1094 (2.91)	31.98	8957	10	−47
TH I-8[m]	–	203	1.820	1231 (2.87)	34.25	9305	15	−52
RDX[n]	–	230	1.816	92.6 (0.42)	35.17	8977	7.4	−22

*Syntheses of all compounds are given in Reference 10a. [a] Melting point. [b] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 10 °C min^{-1}). [c] From gas pycnometer (25 °C). [d] Heat of formation (calculated via Gaussian 03). [e] Calculated detonation pressure (Cheetah 5.0). [f] Calculated detonation velocity (Cheetah 5.0). [g] Impact sensitivity (BAM drophammer). [h] OB = Oxygen balance (%) for $C_aH_bO_cN_d$: $1600 \times (c-2a-b/2)/M_w$, M_w = molecular weight of salt. [i] X-ray density (23 °C). [j] Bis(aminoguanidinium) 1,1'-ethylenebis(5-nitroiminotetrazolate): ref. 1b. [k] Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium]1,1'-ethylenebis(5-nitroimino-tetrazolate): ref. 12. [l] Carbohydrazinium 1,1'-ethylenebis(5-nitroiminotetrazolate): ref. 1b. [m] 1,2,4,5-Tetrazino-3,6-bis(hydrazinium) 1,1'-ethylenebis(5-nitroiminotetrazolate): ref. 1b. [n] Ref. 25.

properties coupled with the rather high thermal and hydrolytic stabilities make these high-nitrogen materials attractive candidates for energetic applications. The oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water; for a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) = $1600 \times (d-2a-b/2)/M_w$ (Table 3). The relatively moderate oxygen balances of **33** and **34** are -35% and -42%, respectively. Incorporation of one additional oxygen atom from the oxyethylene link to the nitroiminotetrazole moiety slightly improves the oxygen balance of the corresponding compounds and may eventually result in higher exothermicities of the combustion and detonation processes.

In summary, oxy 5-nitroiminotetrazolate salts (**31−36**) were synthesized and characterized in order to develop new energetic materials. Oxyamine and cyanogen azide were used as starting materials for the preparation of the oxy aminotetrazole. The latter was converted into oxy nitroiminotetrazole **29** by nitration with 100% nitric acid in a neat reaction. The 1,1'-ethylenebis(oxy)bis(5-nitroiminotetrazolate) salts were fully characterized using IR and multinuclear NMR (^{1}H, ^{13}C, ^{15}N) spectroscopy, elemental analysis and, in some cases, single crystal X-ray structuring was done. Compound **29** is a very sensitive highly energetic compound which should be assigned to the class of primary explosives and should only be handled with appropriate precautions.

Although all of the energetic salts exhibit lower densities (1.577−1.780 g cm^{-3}) than the neutral nitroiminotetrazole **28** (1.805 g cm^{-3}), they have better thermal stabilities. Selected oxy nitroiminotetrazolate salts **33**, **34**, and **36** show good heats of formation (for **33**: 2.78 kJ g^{-1}, **34**: 2.76 kJ g^{-1}, **36**: 2.82 kJ g^{-1}), good detonation pressures (for **33**: 32.20 GPa, **34**: 33.25 GPa, **36**: 29.36 GPa), good detonation velocities (for **33**: 8789 m s^{-1}, **34**: 9030 m s^{-1}, **36**: 8840 m s^{-1}). Calculated detonation values of these compounds are comparable to those of explosives such as RDX (P = 35.17 GPa, D = 8977 m s^{-1}). To compare properties, new energetic salts **38** and **39** based on 1,1'-ethylenebis(5-nitroiminotetrazole) **28** were synthesized and characterized. While the detonation properties of salts derived from precursors **28** and **29** are similar, for salts of **28** the thermal stabilities and impact sensitivities are better than those for **29**, oxy nitroiminotetrazolate salts **31−36**. Finally, all of the new energetic salts are highly endothermic compounds, have high performances and increased thermal or impact sensitivity values in comparison to the neutral compounds **28** and **29** which might be of interest for future applications as environmentally friendly and high-performing nitrogen or oxygen-rich materials.

D. Energetic Mono-, Di-, and Trisubstituted Nitroiminotetrazoles[1a]

Nitroiminotetrazoles are of special interest because they combine both the oxidizer and energetic nitrogen-rich backbone in one molecule. The simple system of 5-(nitroimino)tetrazoles was prepared by treatment of nitroaminoguanidine with KNO_2 and concentrated HCl nearly 60 years ago.[16a,b] In 1957, 1-alkyl substituted 5-nitroiminotetrazole was extensively investigated by two different methods:[16c] 1) direct nitration of 1-methyl-5-aminotetrazole with nitric acid; and 2) reaction of potassium methylnitramine and cyanogen bromide to form methylnitrocyanamide. After interaction of the latter with hydrazoic acid, 1-methyl-5-nitroiminotetrazole was isolated.

The Idaho group has reported the development of mono-, di-, and tri-substituted 5-aminotetrazole compounds has been extended by the utilization of an excellent *in situ* method which involves reactions of cyanogen azide[11] and primary amines[17a] or hydrazines[17b]. Nitration of these aminotetrazoles using 100% nitric acid without solvent has now been shown to form mono-, di- or tri- substituted nitroiminotetrazole derivatives (Scheme 9).

The treatment of aminotetrazole compounds, which were synthesized from primary amines and cyanogen azide, with excess 100% nitric acid,[18] led to good yields [**40** (88%), **41** (89%), **42** (84%), **43** (67%), **44** (64%), **45** (88%), **46** (67%), **47** (74%), **48** (72%)] of

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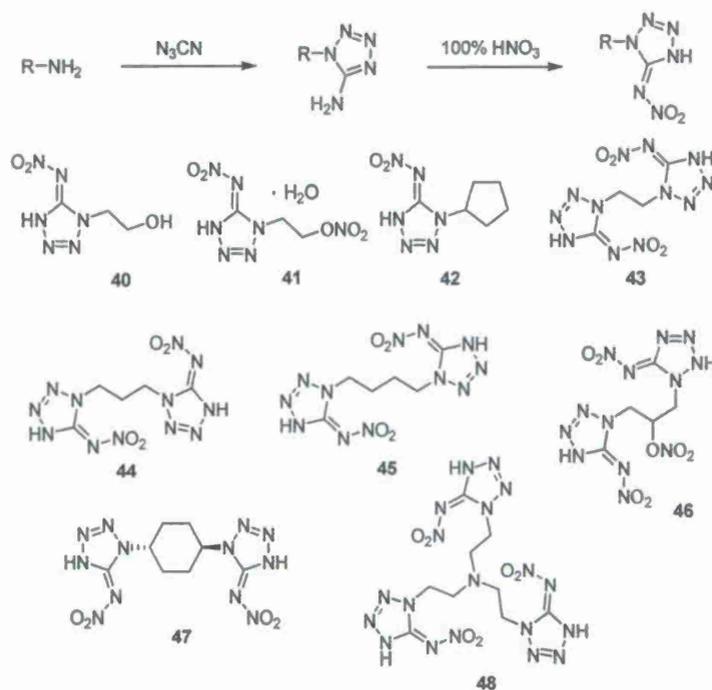
Scheme 9. Synthesis of nitroiminotetrazoles.

nitroiminotetrazoles **40-48**.[19] When the reaction was complete, the reaction mixture was poured into ice water, and stirred for 1–3 hours to give a white solid. In the case of compound **40**, **41** or **42**, the white solid did not precipitate from ice water, but was obtained when the mixture was dried by air. Compounds **40** and **41** were separated by crystallization from water. The structures of **41**, **43** and **48** are supported by IR, and ^{1}H, ^{13}C and ^{15}N NMR spectroscopic data as well as elemental analysis. Single crystals suitable for X-ray determination were obtained from aqueous solution. Structural confirmation of 4,5-dihydro-1-(2-hydroxyethyl)-5-nitroimino-1*H*-tetrazole (**40**) and 1,2-bis(4,5-dihydro-5-nitroimino-1*H*-tetrazol-1-ly)ethane (**43**) was obtained.[20] The colorless crystals are stable at room temperature and are not hygroscopic.

Density is one of the most important physical properties of all energetic materials. As is shown in Table 4, the densities of the new nitroiminotetrazoles range between 1.454 and 1.858 g cm^{-3} (RDX: 1.816; HMX: 1.910 g cm^{-3}). The decomposition temperatures (without melting) fall between 117–233°C [compounds **43**, **44**, **47** and **48** explode at their decomposition temperatures (DSC)]. The heats of formation of the substituted nitroiminotetrazoles **40-48** were computed by using the method of isodesmic reactions. Calculations were carried out by using the Gaussian 03 suite of programs.[9] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G** basis set, and zero-point energies were calculated at the MP2/6-311++G** level. All the 1-substituted nitroiminotetrazoles exhibit positive heats of formation with **43**, **44** and **48** having the highest 3.63, 3.44 and 3.40 kJ g^{-1}.

By using the experimental values for the densities of the nitroiminotetrazoles, **40-48**, the detonation pressures (*P*) and velocities (*D*) were calculated based on traditional Chapman-Jouget thermodynamic detonation theory using Cheetah 4.0 and 5.0.[14] The calculated detonation pressures lie in the range between 17.70 and 38.19 GPa (RDX: 35.17; HMX: 39.63 GPa). Detonation velocities are found in the range between 7358 and 9329 m s^{-1} (RDX: 8977; HMX: 9320 m s^{-1}). For initial safety testing, the impact sensitivity was tested according to BAM methods (BAM Fallhammer).[13] In Table 4, there is a range in impact sensitivities from the insensitive compound **41** (40 J), the sensitive nitroiminotetrazoles (**40**, **42–45,47**, **48**: 10–20 J) and finally to the very sensitive compound **46** (3 J). The impact sensitivities of HMX and RDX are each 7.4 J.[30]

Table 4. Physical properties of nitroiminotetrazoles **40-48** comparing with RDX and HMX.*

Compd	$T_d{}^a$	Density^b	$\Delta_f H°_{298}{}^c$	P^d	vD^e	IS^f	OB
	[°C]	[g cm^{-3}]	[kJmol^{-1} (kJ g^{-1})]	[GPa]	[m s^{-1}]	[J]	[%]
40	158	1.722	258.7 (1.49)	28.23	8465	20	−55.2
41	117	1.712	350.1 (1.60)	30.88	8496	> 40	−23.6
42	124	1.454	398.8 (2.01)	17.70^h	7358^h	20	−121
43	194	1.858	1038.3 (3.63)	38.19	9329	10	−39.1
44	173	1.658	1032.0 (3.44)	28.06	8374	10	−53.3
45	145	1.579	989.6 (3.15)	24.71	7963	15	−66.2
46	139	1.759	922.5 (2.55)	33.02	8741	3	−28.8
47	233	1.564	1022.2 (3.00)	23.61	7667	15	−84.6
48	182	1.616	1649.7 (3.40)	25.96	8185	10	−64.3
RDX^i	230	1.816	92.6 (0.42)	35.17	8977	7.4	−21.6
HMX^i	287	1.910	104.8 (0.35)	39.63	9320	7.4	−21.6

* Syntheses of all compounds are given in Reference 1a. ^{a} Thermal decomposition temperature under nitrogen gas (DSC, 10°C/min). ^{b} Gas pycnometer (25°C). ^{c} Heat of formation (Using 83.68 kJ mol^{-1} for the enthalpy of sublimation for each compound; calculated via Gaussian 03). ^{d} Calculated detonation pressure. ^{e} Calculated detonation velocity. ^{f} Impact sensitivity (BAM drophammer). ^{g} OB = Oxygen Balance (%) for $C_aH_bO_cN_d$: $1600*(c-2a-b/2)/M_w$, M_w = molecular weight of nitroiminotetrazole. ^{h} Using CHEETAH 4.0. ^{i} ref. 14

The physical values of the decomposition temperature, density, oxygen balance, heat of formation (kJ g^{-1}) and detonation properties of **43**, **44** and **45** decrease with increasing number of methylene groups, although their shock sensitivity is essentially constant at 10–15 J.

In summary, with the exception of **46** all of the nitroiminotetrazoles have lower impact sensitivities than RDX or HMX. However, only **43** and **46** have detonation properties which can compete with HMX or RDX, respectively. The enthalpies of formation of the new nitroiminotetrazoles are considerably higher based on kJ/g than either of the latter materials but most have lower thermal stabilities and usually lower oxygen balance.

E. Trinitromethyl-substituted 5-Nitro- or 3-Azo-1,2,4-triazoles[22b]

Of particular interest are high-nitrogen compounds (e. g., azoles) in combination with energetic substituents such as nitro (–NO_2), nitrato (–ONO_2), and nitramine (–$NHNO_2$) functionalities, since these compounds have satisfactory oxygen content.[21] However, the requirements of insensitivity and high energy along with positive oxygen balance are quite often contradictory to each other, making the development of new high energy density materials an interesting and challenging problem.[22a] Polynitro azoles have been a recent focus because of their high performance and low sensitivity to friction and impact.[23-25] Azoles with more than two nitro groups are highly powerful and as a result, a large variety of nitroazoles have been prepared.[26] In reaction of the latter with bases such as ammonia, hydrazine, and guanidine, stable energetic salts are obtained which may hold promise for future applications.[1a,27]

In a continuing effort to seek more powerful, less sensitive, eco-friendly energetic materials, we are interested in heterocyclic compounds that contain a high percentage of both oxygen and nitrogen, and lower amounts of carbon and hydrogen. Heterocyclic compounds with high nitrogen content are environmentally friendly, have high heats of formation, and are endothermic. The high nitrogen content of these compounds often leads to high crystal density which is associated with increased performance. Incorporation of a triazole ring into a compound is a known strategy for increasing thermal stability. Many triazole compounds show high thermal sensitivity coupled with low sensitivity to shock and impact.[28] Here we report the synthesis of various polynitro-1,2,4-triazoles which contain trinitromethyl groups and which display potentially significant physical and energetic properties.

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Aminotriazolylacetic acid (**49**) was synthesized by intramolecular condensation of the malonyl derivative of aminoguanidine bicarbonate in alkaline medium (Scheme 10).[29] Nitration of
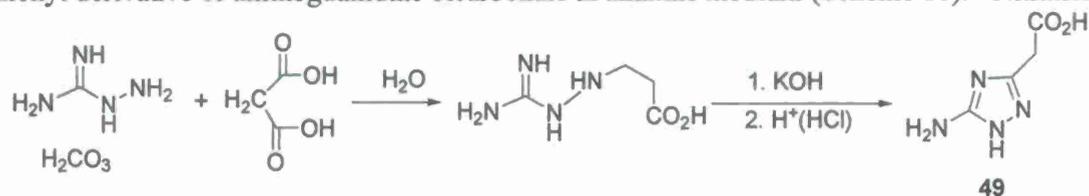
Scheme 10. Synthetic pathway for intermediate **49**.

amino triazole **49** was attempted by using different nitrating methods such as, 70% HNO_3, 100% HNO_3, or mixed acids (HNO_3/H_2SO_4), but the product was not isolable from the reaction mixture. So, a nitro group was thought to be useful in lieu of the 5-amino group. Therefore, amino triazole **49** was converted into corresponding nitro compound **50** by reacting with sodium nitrite and HNO_3 (Scheme 10).[29b] In the reaction of **50** with mixed acids, 5-nitro-3-trinitromethyl-1H-1,2,4-triazole (**51**) was obtained as a single product at ambient temperature.

During this process the proposed intermediate trinitro carboxylic acid was not isolated. The reaction was complete in 12 h. Since no precipitate formed when the reaction mixture was added to ice, the aqueous solution was extracted with dichloromethane resulting, after solvent removal, in a white crystalline product (**51**) in 44% yield (Scheme 11). Potassium salt **52** was
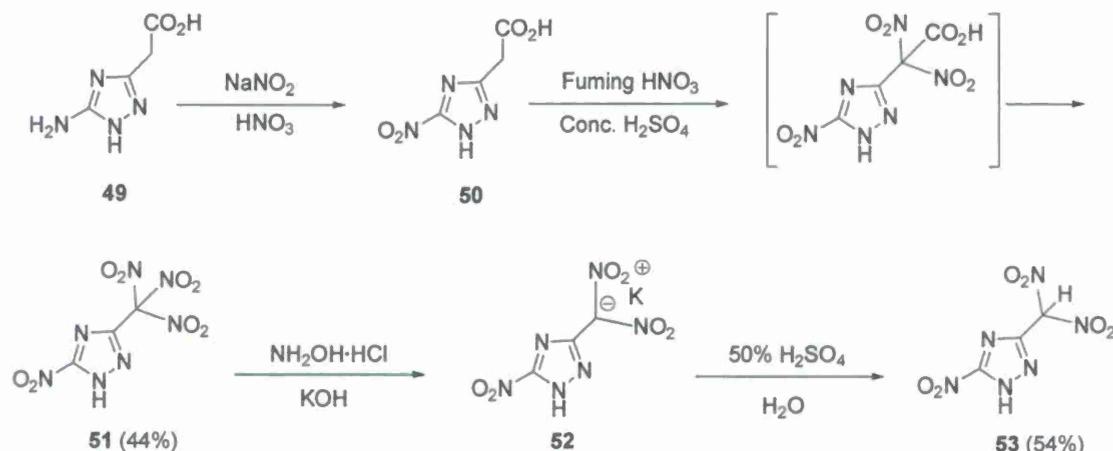
Scheme 11. Synthesis of trinitromethyl (**51**) and dinitromethyl (**53**) 1,2,4-triazoles

btained when **51** was treated with an alkaline solution of hydroxylamine. Acidification with 50% sulfuric acid gave 3-dinitromethyl-5-nitro-1H-[1,2,4]triazole (**53**) as a yellow solid (Scheme 11).

N-Methyl azoles are often less sensitive to impact and friction compared to the corresponding N-H azoles. The methyl derivative was difficult to prepare by reacting with methyl iodide or dimethylsulfate in the presence of bases, e. g., triethyl amine, potassium t-butoxide, potassium hydroxide, or sodium hydride. In all of these cases, low yields of the impure methylated product (**54**) were obtained. When tetranitro **51** was reacted with commercially available trimethylsilyl diazomethane,[29] 1-methyl-5-trinitro-3-trinitromethyl-1H-[1,2,4]triazole (**54**) was obtained in 80% yield (Scheme 12).
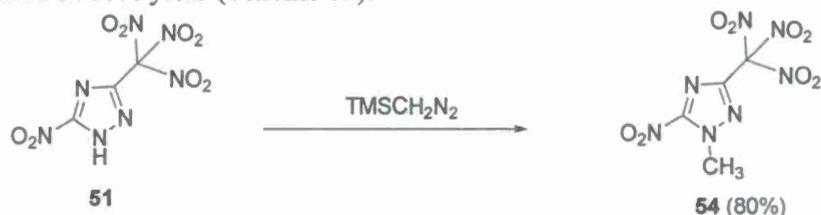
Scheme 12. Methylation of tetranitro **51** to **54**.

Next similar successful attempts were made to synthesize **56** and **57**. The amino triazolylacetic acid **49** was converted into the azo compound, **55**, by treating with alkaline potassium permanganate.[29b] Compound **55** was reacted with mixed acids at room temperature to form 5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole **(56)**. When an attempt was made to convert the trinitromethyl groups of hexanitro **56** to the corresponding dinitromethylene groups by treating with alkaline hydroxylamine followed by acidification, a low yield mixture of compounds was formed. The reaction also failed with potassium iodide in methanol. Methylation of hexanitro **56** was carried out using various reagents; however, reaction was successful with trimethylsilyl diazomethane to produce 1,1'-dimethyl-5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole **(57)** (Scheme 13).

The structures of the new polynitro triazoles are supported by IR, ^{1}H, ^{15}N, and ^{13}C NMR spectroscopic data as well as elemental analysis. In the IR spectra, strong absorption bands at ~1630-1610 cm^{-1} are attributed to the trinitromethyl group. In the ^{13}C NMR spectra, resonance bands for the trinitromethyl group appear between 120-130 ppm. The ^{15}N NMR spectra of the nitrotriazoles were measured in DMSO[D$_6$] solution and chemical shifts are given with respect to CH$_3$NO$_2$ as external standard.
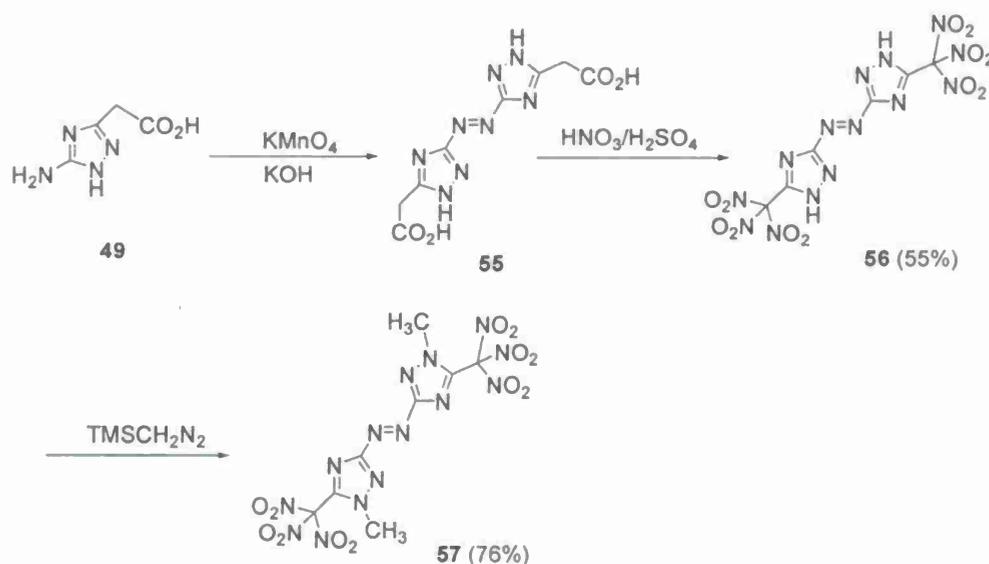
Scheme 13. Synthesis of triazoles **56** and **57**.

Crystals of **54** suitable for single crystal X-ray diffraction, were obtained by dissolving the compound in a minimum amount of methanol, held at 0 °C, followed by filtration of crystals. It crystallizes in an orthorhombic crystal system (space group Pna2$_1$) (Figure 4). The triazole ring and three nitro groups are tetragonally attached to C7. The C-N bond length [1.533(15)] of the trinitromethyl group of **54** is slightly longer than C-N bond length [1.525(3)] of trinitroethyl-containing molecules. This is in agreement with the greater stability of the latter compounds.

As shown in Table 5, the polynitro triazoles exhibit excellent energetic properties. The enthalpies of energetic materials depend on molecular structures of the compounds. Consequently, heterocycles with high nitrogen content exhibit higher heats of formation. All *ab initio* calculations were carried out using the program package Gaussian 03 (Revision D.01).[9] The geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP with the 6-31+G** basis set,[17] and single-point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated by the G2 method. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface

a   b
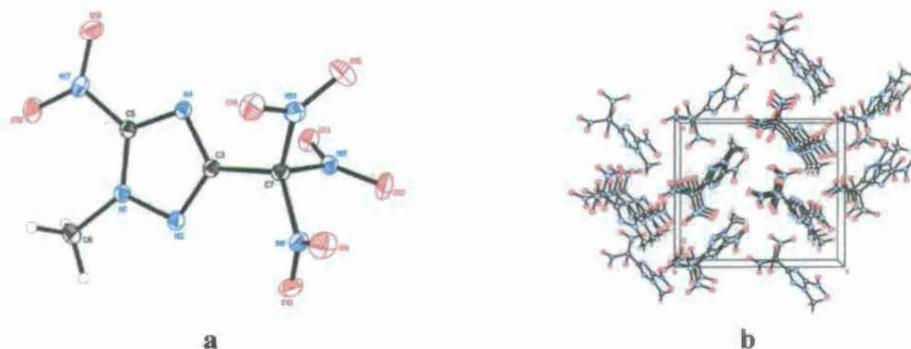
Figure 4. a) A view of the molecular unit of **54.** b) Unit cell view along the *b* axis. Selected bond lengths [Å]: N1-N2 1.3484(15), N1-C5 1.3485(15), N1-C6 1.4684(16), N2-C3 1.3298(16), N4-C5 1.3112(16), C5-N17 1.4555(16), C7-N14 1.5337(15), C7-N11 1.5373(17), N8-O9 1.2122(14), N8-O10 1.2138(15).

without imaginary frequencies. The remaining task is to determine the heats of formation of the polynitro triazoles which are computed by using the method of isodesmic reactions. Thus, the heat of formation of the species being investigated can be easily extracted. All of the polynitro

Table 5. Physical properties of polynitro triazoles.*

Compd	T_m[a] °C	$T_{dec.}$[b] °C	Density[c] g cm^{-3}	OB[d] %	O[e] %	ΔH_f^o[f]kJ/mol (kJ/g)	IS[g] J	P[h] GPa	D[i] m/s	I_{sp}[j] s
51	113	135	1.94 (1.92)[k]	+9.12	48.7	123.2 (0.46)	9.0	35.51	8983	233
53	-	87	1.91 (1.85)	-7.33	44.0	84.1(0.38)	9.5	38.41	9229	243
54	77	153	1.88 (1.88)	-3.46	46.2	95.6 (0.34)	13	36.88	9006	264
56	-	150	1.83 (1.87)	-8.6	41.5	555.1 (1.20)	1.5	36.65	8964	264
57	-	165	1.78 (1.77)	-22.8	39.2	505.8 (1.03)	5.5	33.83	8742	262
TNT	81	295	1.65	-74	42.3	-67.0 (0.30)	15	19.53	6881	-
RDX	dec	230	1.82	-21.6	43.2	92.6 (0.42)	7.4	35.17	8997	-
HMX	dec	287	1.91	-21.6	43.2	104.8 (0.35)	7.4	39.63	9320	-

* Syntheses of compounds are given in Reference 22b. [a] Melting point. [b] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5°C/min^{-1}). [c] Gas pycnometer (25 °C). [d] OB = Oxygen balance (%) for $C_aH_bO_cN_d$: 1600 × (c–2a–b/2)/M_w, M_w = molecular weight of compound. [e]Oxygen content. [f] Heat of formation (Gaussian 03, Revision D.01). [g] Impact sensitivity (BAM drophammer). [h] Detonation pressure (Cheetah 5.0). [i] Detonation velocity (Cheetah 5.0). [j] Specific impulse (Cheetah 5.0). [k] Calculated density, Ref. 31.

triazoles exhibit positive heats of formation and are comparable to or greater than those of TNT, RDX, and HMX. Compound **51** is far superior to ADN in all respects, including detonation velocity and pressure, enthalpy of formation, impact sensitivity, and density, with the exception of oxygen balance although **51** is positive at 9% compared to 25.8% for ADN.[29] The densities of these compounds are in the range of 1.78-1.94 g/cm^3 which equals or exceeds that of common explosives. Tetranitro triazole (**51**) has the highest density at 1.94 g/cm^3. The calculated densities are in good agreement with the experimentally determined values (Table 5).[31]

Impact sensitivity measurements were made using standard BAM Fallhammer techniques.[13] For all of the compounds, the impact sensitivities range from those of the relatively less sensitive **51, 53, 54,** and **57** between 5.5 to 13 J to the very sensitive compound **56** (1.5 J). *N*-methyl derivatives (**54** and **57**) are less sensitive than the corresponding *N*-H compounds **51** and

56. Thermal stabilities of the energetic compounds were determined with differential scanning calorimetry (DSC) at a scan rate of 5 °C min^{-1}. Compound **51** melted at 113 °C and decomposed at 135 °C, whereas its methyl derivative (**54**) melted at 77 °C and decomposed at 153 °C. Azo compounds **56** and **57** decomposed at 150 °C and 165 °C, respectively, without melting. Surprisingly, the trinitro compound **53** decomposed at 87 °C which is thermally less stable than the tetranitro compound **51**.

By using the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer, 25 °C) of the new energetic polynitro triazoles, the detonation pressures (P) and detonation velocities (D) were calculated based on traditional Chapman-Jouget thermodynamic detonation theory using Cheetah 5.0 (Table 5).[14] The detonation pressures of polynitro triazoles lie in the range between $P = 33.83$ to $P = 38.41$ GPa (compared with TNT 19.53 GPa, RDX 35.2 GPa and HMX 39.6 GPa). Detonation velocities lie between $D = 8742$ and $D = 9229$ m s^{-1} (compared with TNT 6881 m s^{-1}, RDX 8997 m s^{-1} and HMX 9320 m s^{-1}). The specific impulse values (CHEETAH 5.0) of these polynitrotriazoles which range between 233 to 264s suggest propellant possibilities. The calculated properties coupled with the rather high thermal and hydrolytic stabilities suggest that these high nitrogen, oxygen-rich materials may be attractive candidates for energetic applications.

Oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water; for a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) = (d-2a-b/2)/MW (Table 5). Positive oxygen balance has significance in explosives which can be used as oxidizers. Compound **51** has a positive oxygen balance of 9.1%; the oxygen balances of **53**, **54** and **56** are -7.3, -3.6, and -8.6%, respectively, which are superior to RDX (-22%) and HMX (-22%). The oxygen percentages of **51**, **53**, and **54** are 48.7, 44.0, and 46.2%, respectively, which are superior to TNT (42.26%), RDX (43.22%), and HMX (43.22%) and nearly competitive with AP.

In summary, the syntheses of high energy density polynitro triazoles, 5-nitro-3-trinitromethyl-1H-[1,2,4]triazole) (**51**), 3-dinitromethyl-5-nitro-$1H$-[1,2,4]triazole (**53**), 1-methyl-5-nitro-3-trinitromethyl-$1H$-[1,2,4]triazole (**54**), 5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole (**56**), and 1,1'-dimethyl-5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole (**57**) were carried out and their physical and detonation properties were determined. These compounds exhibit good physical and detonation properties, such as moderate thermal stabilities, high densities, high heats of formation, and high detonation pressures and velocities. Calculated detonation values for these compounds are comparable to those of explosives such as TNT, RDX, and HMX. Tetranitro triazole **51** has a positive oxygen balance, 48.7% oxygen content and a decomposition temperature of 135 °C which suggests its use as a new stable oxidizer. In all aspects, except for oxygen balance, it is far superior to ADN. The other triazoles have good oxygen balance that is superior to RDX and HMX. The N-methylated compounds are less sensitive than the corresponding N-H triazoles. Triazoles **51**, **53**, and **54** are less sensitive than RDX and HMX which suggests that these compounds might be of interest for future applications as environmentally friendly and high-performing nitrogen or oxygen-rich materials and may serve as a series of promising alternatives to RDX and HMX.

F. 1-Amino-1-hydrazino-2,2-dinitroethene and its salts

1,1-Diamino-2,2-dinitroethene (DADNE) or FOX-7 (**58**) has a highly polarized carbon–carbon double bond with positive and negative charges being stabilized by the two amino groups and the two nitro groups, respectively.[32] The existence of **58** in a variety of tautomers and resonance structures[32,33] suggests the possibility of reactions with both nucleophiles and electrophiles enabling design and optimization of FOX-7 molecular structures in order to enhance performance with respect to sensitivity.[34]

1-Amino-1-hydrazino-2,2-dinitroethene (**59**) was synthesized by the reaction of the potassium salt of 1,1-diamino-2,2-dinitroethene (DADNE) or FOX-7, **58**, with hydrazine hydrate in ethanol (Scheme 14).[35,36] The presence of the hydrazino-group in **59** will increase the heat of

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formation of the entire molecule;[37] however, the literature reports that **59** undergoes spontaneous energetic decomposition.[38] The authors warn emphatically that **59** should be handled with extreme caution. Apparently due to this reason, in addition to its hydrazinium salt (**51**), limited derivatives of **59** have been synthesized and the only information which is available is their IR, and NMR spectra, and decomposition temperatures.[39]

Recently, considerable effort has focused on syntheses of new energetic salts with higher performance and/or lower sensitivity as well as environmental compatibility. Energetic salts often possess advantages over neutral molecules since these salts usually have lower vapor pressures and higher thermal stabilities than their similar nonionic analogues. It was of value to study the other properties (such as detonation properties and thermostability) of 1-amino-1-hydrazino-2,2-dinitroethene (**59**) and its hydrazinium salt (**60**). In addition, it was of interest to form salts with other cations to tune the properties of **59** in order to improve the sensitivity and thermal stability.

In our work, the potassium salt of 1-amino-1-hydrazino-2,2-dinitroethene (**61**) was synthesized for the first time (Scheme 14). With **61** as starting material, **59** was prepared by acidifying its aqueous solution. Then by treating **59** with hydrazine hydrate or guanidine carbonate, **60,** and guanidinium 1-amino- 1-hydrazino-2,2-dinitroethene (**62**) were synthesized.

The structures of **59** and its salts **60-62** are supported by IR, and ^{1}H, ^{13}C, and ^{15}N NMR spectroscopic data as well as from elemental analysis. Structural confirmation of the potassium, hydrazinium, and guanidinium salts of **59** was obtained by single crystal X-ray diffraction analyses.

Crystals of **60** and **62**, suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of aqueous solutions at room temperature. Their structures are shown in Figures 5 and 6. Single-crystal X-ray diffraction analysis show that compounds **60**, and **62** crystallize in the monoclinic space group P2(1)/n, and triclinic space group P-1, respectively. The transfer of
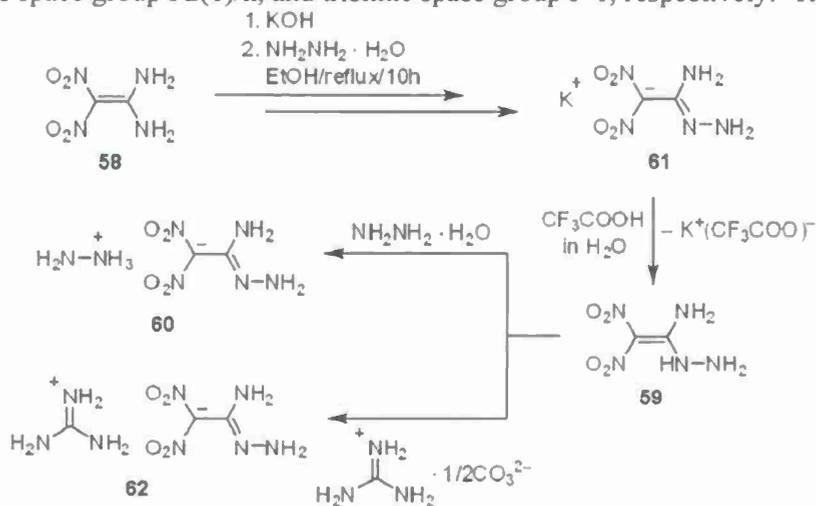
Scheme 14. Synthesis of 1-amino-1-hydrazino-2,2-dinitroethene and its salts

each proton from the NH group of **59** to hydrazine and guanidine is confirmed in Figures 5 and 6.

Thermal stabilities of **59** and its salts **60, 61** and **62** were determined by differential scanning calorimetric (DSC) measurements (Table 6). Compounds **59-62** decomposed without melting at 124.5 (**59**), 138.6 (**60**), 181.6 (**61**) and 157.9 °C (**62**), respectively. Density is one of
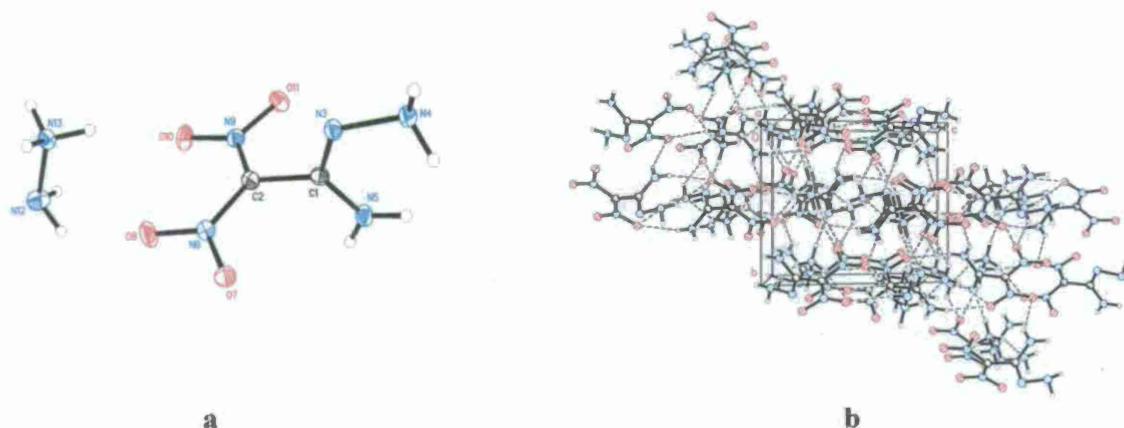
Figure 5. a) Thermal ellipsoid plot (30%) and labeling scheme for the hydrazinium salt of 1-amino-1-hydrazino-2,2-dinitroethene (**60**). Hydrogen atoms included but are unlabelled for clarity. b) Ball and stick packing diagram of **60** viewed down the a axis. Dashed lines indicate strong hydrogen bonding.
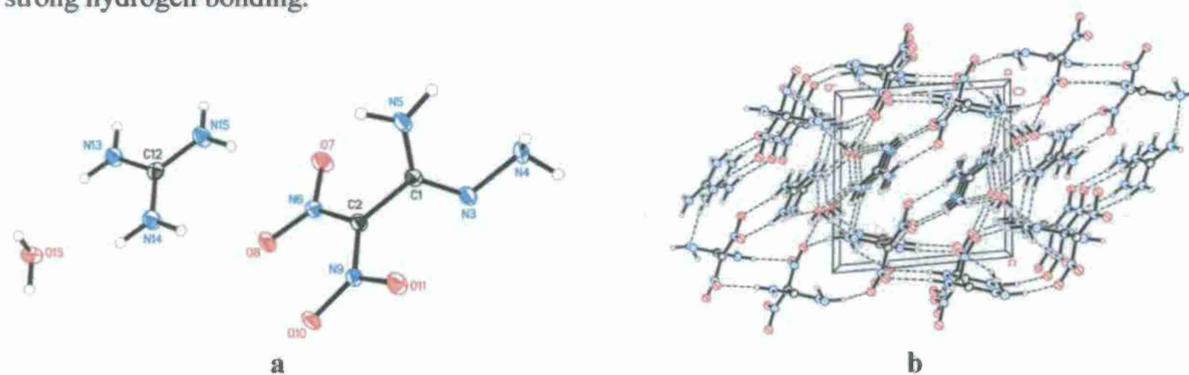
Figure 6. a) Thermal ellipsoid plot (30%) and labelling scheme for the guanidinium salt of 1-amino-1-hydrazino-2,2-dinitroethene (**62**). Hydrogen atoms included but are unlabelled for clarity. b) Ball and stick packing diagram of **62** viewed down the a axis. Dashed lines indicate strong hydrogen bonding.

the most important physical properties of all energetic materials. Given in Table 6 are densities of **59-62** measured with a gas pycnometer and found to range between 1.56 (**62**) and 1.92 g cm⁻³ (**61**) (RDX: 1.82; HMX: 1.91 g cm⁻³) .

Compound **59** is a dangerous energetic material which was found to undergo spontaneous energetic decomposition which can lead to damage.[36] In our research, when the newly prepared **59** was placed on filter paper to dry at room temperature in air, the compound decomposed spontaneously and ignited the paper. We strongly recommend using **59** immediately after synthesis and avoiding storage.

Based on our calculations using the Gaussian 03 (Revision D.01) suite of programs,[9] the heat of formation, which is one of the important characteristics for energetic salts, was obtained. The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G** basis set, and single-point energies were calculated at the MP2/6-311++G** level. The calculated $\Delta_f H$ for the 1-amino-1-hydrazino-2,2-dinitroethene anion is 465.9 kJ/mol which is highly positive due to its high nitrogen content. This also results in positive $\Delta_f H$ for all compounds in the range of 71.6 (**59**) to 721.9 kJ/mole (**62**). The standard enthalpies of formation ($\Delta_f H$) for all compounds were calculated by using Born-Haber energy cycles

With the data for the experimental values found for the densities, calculated heats of formation and the empirical formulae for **59–62**, the detonation pressure (P) and velocity (vD), and specific impulse (Isp) values of **59–62** were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using Cheetah 5.0.[14] Based on the data in Table 6, the

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Table 6. Physical properties of compounds **59–62**.*

	d^a	T_d^b	$\Delta_f H_{cation}{}^c$	$\Delta_f H_{anion}{}^d$	$\Delta H_L{}^e$	$\Delta_f H^f$	P^g	vD^h	IS [J]^i	OP %
59	1.78	124.5	-	-	-	0.44	33.8	8803	6	39
60	1.67	138.6	575.9	465.9	488.2	2.82	37.8	9482	11	32
61	1.92	181.6	501.1	465.9	529.1	2.18	37.3	8973	10	33
62	1.56	157.9	770	465.9	514.0	3.25	27.2	8424	25	29

* Syntheses of all compounds are given in Reference 41. ^{a} Density [g cm^{-3}]; ^{b} Decomposition temperature [$^{\circ}$C]; ^{c} Heat of formation of cation [kJ mol^{-1}]; ^{d} Heat of formation of anion [kJ mol^{-1}]; ^{e} Lattice energy [kJ mol^{-1}]; ^{f} The heat of formation [kJg^{-1}]; ^{g} Detonation pressure [GPa]; ^{h} Detonation velocity [ms^{-1}]. ^{i} Impact sensitivity (BAM drophammer). ^{j} **59** in the condensed phase is estimated with the assumption that its enthalpy of sublimation is 84 kJ/mol.

calculated detonation pressures and velocities fall in the range of 27.2–37.8 GPa and 8424–9482 ms^{-1}, which are superior to that of trinitrotoluene (TNT 19.5 GPa and 6881 ms^{-1}). Compound **59** with a detonation pressure and velocity of 37.8 GPa and 8543 ms^{-1}, and salt **60** with a detonation pressure and velocity of 37.3 GPa and 8973 ms^{-1}, are values much higher than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, 31.15 GPa and 8114 ms^{-1}), and comparable with RDX (35.2 GPa and 8977 ms^{-1}) and HMX (39.6 GPa, 9320 ms^{-1}).[30] Impact sensitivities of all of the compounds were measured by using a BAM Fallhammer apparatus with a 2.5 kg (for salts **59, 60,** and **61**) or a 10 kg (for salt **62**) drop weight. It was found that **59** is the most sensitive at 6 J which is more sensitive than HMX and RDX (7.4 J).[30] Salts **60** and **61** with similar sensitivities 11 and 10 J are slightly more sensitive than TNT (15 J).[40] The sensitivity of **62** is 25J which is the lowest among all four compounds.

In summary, three energetic salts based on 1-amino-1-hydrazino-2,2-dinitroethene anions and a molecular species (**59**) were prepared and fully characterized. The structures of **60, 61** and **62** were confirmed by single-crystal X-ray diffraction, which showed that there are extensive hydrogen-bonding interactions between the cation and anion in these salts. Densities for these salts, measured with a gas pycnometer, were found to fall in the range between 1.56 (**62**) and 1.92 g cm^{-3} (**61**), which places them in a class of relatively dense compounds. By using Cheetah 5, their detonation pressures and velocities were calculated to fall between 27.2–37.8 GPa and 8424–9482 ms^{-1}. Salts **60** and **61**, with detonation pressures and velocities higher than 37.0 GPa and 8900 ms^{-1}, are comparable with RDX (35.2 GPa and 8977 ms^{-1}) and HMX(39.6 GPa, 9320 ms^{-1}).[16] With the exception of **62** (25 J), the impact sensitivities of the 1-amino-1-hydrazino-2,2-dinitroethene salts are ~10 J. Based on rather high detonation properties, the 1-amino-1-hydrazino-2,2-dinitroethene salts have potential as energetic materials.

G. Synthesis and promising properties of a new family of high-density energetic salts of 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole and 5,5'-bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole[42]

Recently, we reported the synthesis of trinitromethyl-substituted triazoles, 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole (**51**) and 5,5'-bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole (**56**).[22b] The salts of these compounds are likely to exhibit high density and detonation properties and be insensitive energetic materials. To the best of our knowledge, energetic salts of C-trinitromethyl-substituted azoles which have acidic *N*-H bonds along with their energetic properties were unknown. In this paper, we reported the synthesis of various high density energetic salts of polynitro-1,2,4-triazoles which contain trinitromethyl groups and which display potentially significant physical and energetic properties.

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Azoles containing active methylene groups can be converted into corresponding nitromethyls by reacting with mixed acids (fuming nitric acid and concentrated sulfuric acid). Azolylacetic acids give trinitromethyl-substituted compounds in one-pot reactions.[22b] 5-Amino-1,2,4-triazolyl-5-acetic acid (49) was prepared by the condensation of aminoguanidine bicarbonate and malonic acid. The amine group of 49 was converted into a nitro group by reacting with sodium nitrite in acidic medium. Nitration using mixed acids produced trinitromethyl triazole, 51. Similarly, the azo-compound 55 which was prepared by reacting aminotriazole 49 with potassium permanganate was converted to the corresponding trinitromethyl compound 56 by mixed acid nitration (Scheme 15) .[22b,29]
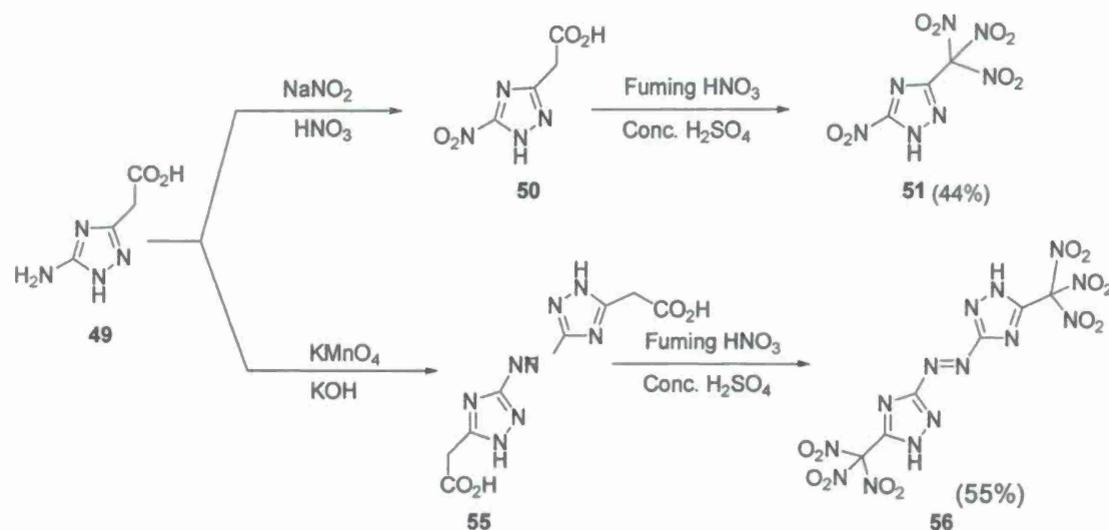
Scheme 15. Synthetic pathways for trinitromethyl-substituted triazoles **51** and **56**.

5-Nitro-3-trinitromethyl-1H-1,2,4-triazole (51) has an oxygen content of 48.7% with positive oxygen balance (+9.12) and a positive heat of formation (123.2 kcal mol^{-1}).[22b] Reactions of tetranitro triazole 51 with 3,4,5-triamino triazole, bis(guanidinium) tetrazine, and ammonia, resulted in the formation of salts 63, 64, and 65 (Scheme 16). Reaction of 51 with excess ammonia also produced the mono ammonium salt 65. Reaction of 51 with one molar equivalent of hydrazine or hydroxylamine produced impure mixtures of compounds. Increasing the molar equivalents of hydrazine and hydroxylamine vis-à-vis 51 produced the dihydrazinium (66) and dihydroxylammonium (67) salts, respectively. Interestingly one of the nitro substituents of the trinitromethyl group was displaced in addition to the N-1 hydrogen of the triazole ring to form dications in the latter two reactions. It may be that hydrazine and hydroxylamine are more nucleophilic than ammonia (Scheme 16).

Reactions of 5,5'-bis(trinitromethyl)-3,3'-azo-1H-1,2,4-triazole (56) with two moles of 3-aminotriazole, 3,4-oxadiazole, diamino urea, 3,4,5-triamino 1,2,4-triazole, and bis(guanidinium) tetrazine resulted in the formation of dianionic salts 68-72. All of the salts are non hygroscopic, stable in air, and were isolated as crystalline materials in good yields. The reaction of hexanitro triazole, 56, with hydrazine or hydroxylamine produced a mixture of compounds (Scheme 17). The structures of the new salts were determined by ^{1}H, and ^{13}C NMR (some salts with ^{15}N NMR), and IR spectroscopy, and elemental analysis. In the ^{1}H NMR spectra, the hydrogen signals of the cations were observed and easily assigned since there are no protons associated with the anions of triazoles 51 and 56. In the IR spectra, several main absorption bands around 1540, 1480, 1420, and 1310 cm^{-1} are attributed to the triazole anions. The intense bands in the range of 1600-1630 cm^{-1} can be assigned to the trinitromethyl groups. In the ^{13}C NMR spectra, resonance bands for the trinitromethyl group appear between 120-130 ppm. ^{13}C NMR chemical shift of the
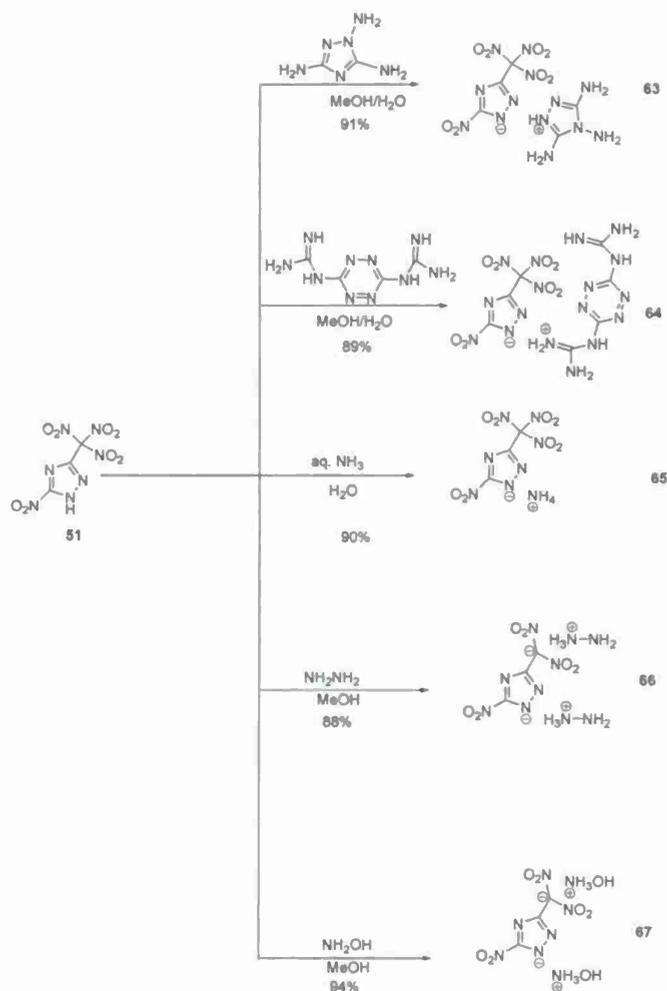
Scheme 16. Synthesis of energetic salts of 5-nitro-3-trinitromethyl-1H-1,2,4-triazole (**51**).

dinitromethyl group of salts **66** and **67** appeared downfield compared to trinitromethyl compounds.[19b] The ^{15}N NMR spectra of the salts of tetranitro triazole (**51**) were measured in DMSO[D$_6$] solution and chemical shifts are given with respect to CH$_3$NO$_2$ as external standard. As in the parent tetranitro triazole, **51,** the anionic triazole nitrogen signals are seen upfield relative to the nitro and trinitromethyl groups with the N2 signal of the triazole ring downfield relative to N3 and N1. The N3 nitrogen resonance falls between N2 and N1. Based on comparison with the literature, the chemical shifts of the hydroxylamine, hydrazine moieties, and $^+$NH$_3$ groups can be assigned to the resonances at highest field.[10a] The salts of hexanitro triazole, **56,** are only slightly soluble in organic solvents including DMSO[D$_6$] and thus it was not possible to obtain ^{15}N spectra. The salts decomposed when heated in DMSO[D$_6$].

The N-methylated derivative of tetranitro **51** has been studied by X-ray crystallography.[22b] But X-ray structures of hexanitro triazole **56** or its derivatives are unknown. The preparation of crystals of **56** suitable for X-ray diffraction analysis was unsuccessful. Therefore, an attempt was made to prepare co-crystals of **56** with amine-substituted triazoles.

Co-crystallization of different components represents supramolecular synthesis where hydrogen bonds link molecules. Co-crystals are different from solid solutions or mixed crystals and can be considered as molecular complexes. The donor and acceptor functionalities can be
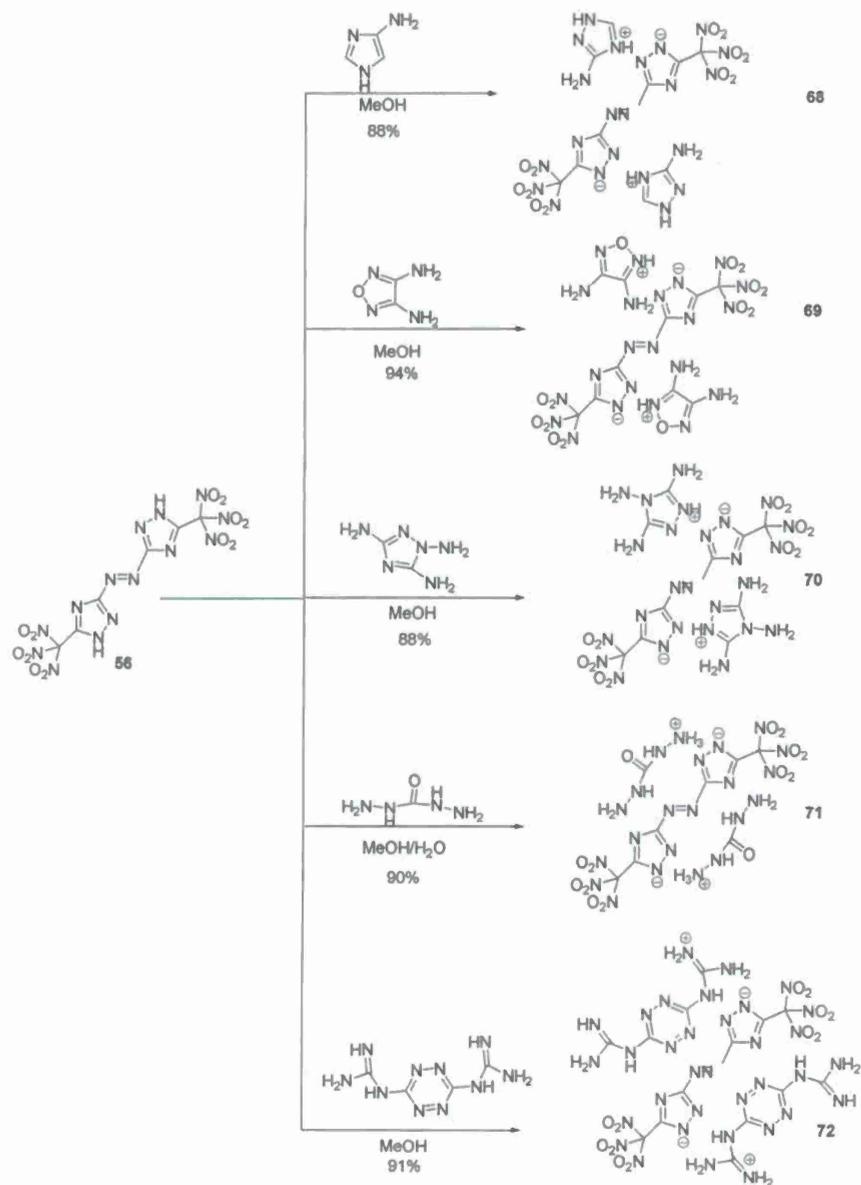
Scheme 17. Synthesis of energetic salts of 5,5'-bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole (**56**).

brought together more easily than with single component systems because the partners are more accessible to arrange themselves into an optimal geometry, leading to favorable intermolecular interactions. 3-Amino-1,2,4-triazole, 4-amino-1,2,4-triazole, and 3,5-diamino-1,2,4-triazole were used in attempts to prepare co-crystals with hexanitrotriazole, **56**. Through N-H...O interactions, triazole **56** formed co-crystals with 3,5-diamino-1,2,4-triazole only when equimolar amounts were dissolved in a mixture of 1:1 water:methanol (**73**).

Cocrystal **73** has a crystallographic density of 1.67 g cm^{-3} at 100 K which is somewhat lower than the parent hexanitro triazole **56**. A significant decrease in the decomposition temperature of **56** was observed with cocrystal **73** decomposing at 120 °C. Incorporating insensitive 3,5-diamino-1*H*-1,2,4-triazole into a cocrystal with hexanitro **56** greatly reduces its impact sensitivity from 1.5 J to 9.0 J, potentially improving the viability of **56** in explosive applications.

The co-crystals obtained were suitable for single crystal X-ray diffraction determination; it crystallizes in a triclinic crystal system (space group P-1) (Figure 7). The N-N bond length of

a   b
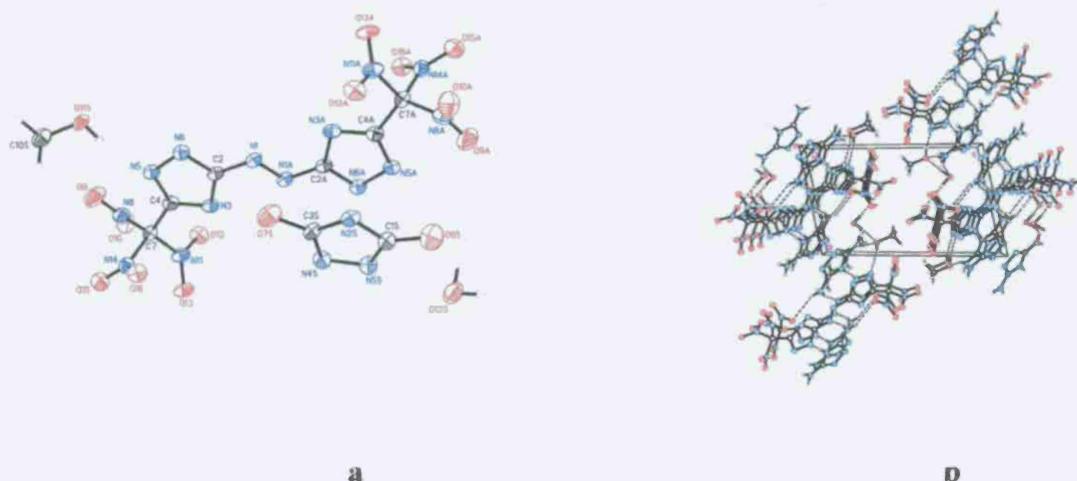
Figure 7. a) A view of the molecular unit of co-crystal **73.** b) Unit cell view along the *b* axis. Selected bond lengths [A]: N5-N6 1.342(10), C2-N6 1.320(11), C2-N3 1.366(12), N3-C4 1.327(12), N1-C2 1.387(12), C4-C7 1.465(14), C7-N14 1.524(13), N11-O12 1.216(11).

the azo bridge is 1.242 (13) A, which is shorter than N5-N6 bond lengths of the triazole ring [1.342(10)]. The triazole ring and three nitro groups are tetragonally attached to C7. The C-N bond length of trinitromethyl is 1.556(15) which is longer than C-N bond length [1.525(5)] of trinitroethyl-containing molecules. Each cation can form a variety of hydrogen bonds. The extensive hydrogen-bonding interactions between the two molecules form a complex 3D network.

In Table 7 is shown that trinitromethyl-subsitituted triazole salts are highly endothermic compounds. The enthalpies of energetic materials are controlled by the molecular structure of the compounds. Consequently, heterocycles with higher nitrogen content (such as triazole), show higher heats of formation. All the new compounds (except dinitromethyl salts **66** and **67**) exhibit positive heats of formation ranging between 74.0 and 1630 kJ mol^{-1}. Impact sensitivity measurements were made using standard BAM Fallhammer techniques.[28] Listed in Table 7 are impact sensitivities ranging between 4.5 J and 15.0 J. The thermal stabilities of the salts were determined by differential scanning calorimetric (DSC) measurements and all of the salts decomposed without melting. Decomposition temperatures for salts of **51** range between 130 to 172 °C; dianionic salts **66** and **67** have good thermal stabilities compared to mono anionic compounds **63, 64,** and **65.** The decomposition temperatures of salts of **56** are lower compared to salts of **51** and range from 111 to 140 °C.

As one of the important physical properties of energetic salts, densities of all the salts prepared were measured by using a gas pycnometer (Table 7) and found to fall in the range of

Table 7. Physical properties of polynitro triazole compounds, **63–73.***

compd	$T_{dec.}$[a] °C	Density[b] g cm^{-3}	ΔH_f[c] cation kJ/ mol	ΔH_f[c] anion kJ/mol	Lattice energy[e] kJ/ mol	ΔH_f[oc] kJ/mol (kJ/g)	P[d] GPa	D[e] m/ s	IS[f] J	OB[g] %
51	135	1.94	-	-	-	123.2 (0.46)	35.5	8983	9.0	9.1
56	150	1.83	-	-	-	555.1 (1.20)	36.6	8964	1.5	-8.6
63	145	1.80	877.6	-76.67	442.3	358.6 (0.95)	30.7	8306	9.5	-38.1
64	132	1.81	1124.7	-76.67	421.7	626.4 (1.36)	28.5	8197	10.0	-52.2
65	130	1.78	626.4	-76.67	475.7	74.0 (0.26)	32.4	8475	4.5	-11.4
66	156	1.82	770.0	-693.7	1387.7	-541.4 (-1.91)	30.8	8560	12.0	-56.7
67	172	1.80	669.5	-693.7	1404.7	-759.4 (-2.67)	32.6	8575	10.5	-35.5
68	117	1.70	806.3	310.1	994.4	928.2 (1.47)	26.8	7916	12.5	-45.6
69	140	1.76	935.0	310.1	988.7	1191.3 (1.80)	30.3	8310	13.0	-38.6
70	118	1.70	877.6	310.1	959.6	1105.6 (1.60)	26.6	8053	15.0	-50.9
71	111	1.80	663.0	310.1	1009.4	626.6 (0.97)	32.1	8542	9.0	-39.8
72	113	1.94	1124.7	310.1	929.4	1630.2 (1.90)	36.2	8997	14.5	-97.3
73	120	1.67	-	-	-	-	-	-	9.0	-
TNT	295	1.65	-	-	-	-67.0 (0.30)	19.5	6881	15	-74.0
RDX	230	1.82				92.6 (0.42)	35.1	8997	7.4	-21.6

*Syntheses of all compounds are given in Reference 42. [a] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). [b] From gas pycnometer (25 °C). [c] Heat of formation (calculated via Gaussian 03). [d] Calculated detonation pressure (Cheetah 5.0). [e] Calculated detonation velocity (Cheetah 5.0). [f] Impact sensitivity (BAM drophammer). [g] OB = oxygen balance (%) for $C_aH_bO_cN_d$: $1600\times(c-2a-b/2)/M_w$, M_w = molecular weight of salt.

1.70–1.94 which is expected based on the high density of **51.** Bis(guanidinium)tetrazine salt (**72**) exhibited the highest density at 1.94 g cm^{-3}. These relatively high densities are presumably caused by the high symmetry of the anion and the extensive intra- and intermolecular hydrogen bonds found in these salts.

By using calculated values of the heats of formation and experimental values for densities (gas pycnometer, 25 °C) of the new energetic polynitro triazole salts, the detonation pressures (P) and detonation velocities (D) were calculated using the EXPLO5 program (version 5.05). The detonation pressures of polynitro triazoles lie in the range between $P = 26.8$ to $P = 36.2$ GPa (compared with TNT 19.53 GPa, and RDX 35.2 GPa and HMX 39.6 GPa). Detonation velocities lie between D = 7916 and D = 8997 m s^{-1} (compared with TNT 6881 m s^{-1}, RDX 8997 m s^{-1} and HMX 9320 m s^{-1}). The calculated properties coupled with the rather high thermal and hydrolytic stabilities suggest that these high nitrogen, oxygen-rich materials may be attractive candidates for energetic applications. The oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water; for a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) = $1600\times(d-2a-b/2)/M_w$ (Table 7). The relatively moderate oxygen balance of **65** is −11.4%.

In summary, high density energetic salts of trinitromethyl substituted triazoles, 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole (**51**) and 5,5'-bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole (**56**), were synthesized using straightforward methods. Single crystal X-ray structuring supports the formation of the co-crystal of 5,5'-bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole with 3,5-diamino-1,2,4-triazole which was found to be markedly less impact sensitive than the azo precursor. Physical and detonation properties were determined. These trinitromethyl substituted energetic salts were fully characterized using IR and multinuclear ^{1}H, ^{13}C NMR (some cases ^{15}N NMR) spectroscopy, and elemental analysis. These salts exhibit good physical and detonation properties, such as moderate thermal stabilities, high densities, moderate to high heats of formation, and high detonation pressures and velocities. Calculated detonation values for these compounds are comparable to those of explosives such as TNT, and RDX. The salts of **56** are impact insensitive (9.0–15.0 J) compared to their molecular precursor (1.5 J). They are less sensitive than or comparable to RDX which suggests that they could be of interest for future applications as environmentally friendly and high-performing nitrogen and oxygen-rich materials.

H. 3,4,5-Trinitropyrazole-based energetic salts.[45]

3,4,5-Trinitropyrazole (HTNP) was prepared from the nitration of pyrazole with fuming nitric acid, followed by thermal rearrangement of N-nitropyrazole in benzonitrile, amination with 1,1,1-trimethylhydrazinium iodide, and finally oxidation with 30% hydrogen peroxide (Scheme 18).[43,44]
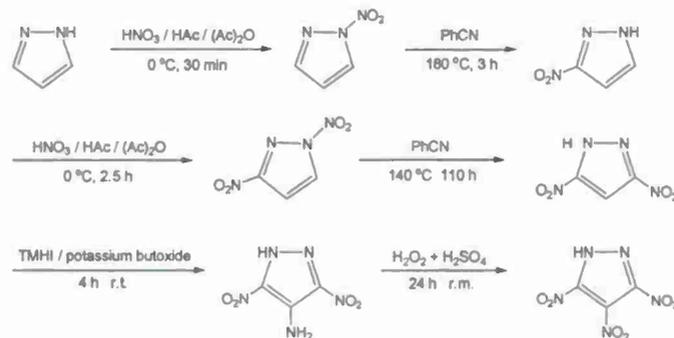
Scheme 18. Synthesis of 3,4,5-trinitropyrazole

Reactions of HTNP with ammonia, triazole, 3-aminotriazole, 4-aminotrizole, 3,5-diaminotriazole, guanidine carbonate, aminoguanidine bicarbonate, and 3,6-diguanidinotetrazine, resulted in the formation of salts **74-81** (Scheme 19). Other salts
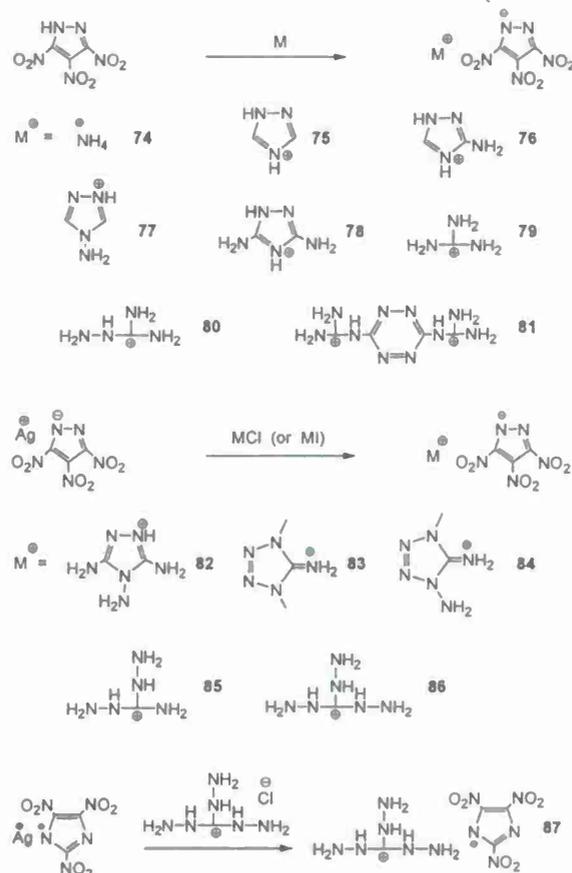
Scheme 19. Synthesis of energetic 3,4,5-trinitropyrazolate and triaminoguanidinium 2,4,5-trinitroimidazolate salts.

82-87 were readily synthesized by metathetical reactions of 3,4,5-triaminotriazolium chloride, 1,4-dimethyl-5-aminotetrazolium and 1,5-diamino-4-methyltetrazolium iodide, and diaminoguanidium and triaminoguanidinium chlorides with Ag(TNP) [or Ag(TNI), silver trinitroimidazolate] which was obtained from treatment of KTNP (or KTNI) with an equivalent amount of aqueous silver nitrate. All the salts which were isolated as crystalline materials in good yields are non hygroscopic and stable in air. Unfortunately attempts to isolate the corresponding trinitropyrazolate salt of 1,5-diaminotetrazole (DAT) were unsuccessful due to the extreme hygroscopicity of the product which became a highly sticky material when exposed to air for several seconds. The structures of the salts **74-87** were supported by ^{1}H, and ^{13}C, and some with ^{15}N, NMR, and IR spectra, and elemental analysis. In the ^{1}H NMR spectra, the hydrogen signals of the cations were observed and easily assigned since there is no proton on the TNP anion. In the ^{13}C NMR spectra, except for two very weak signals (~122 and 147 ppm) assigned to the TNP anion, the other signals are associated with the cations.

In the IR spectra, several main absorption bands around 1520, 1360, 1320, and 850 cm^{-1} are attributed to the TNP anion. The intense absorption bands in the range of 3100-3500 cm^{-1} can be assigned to the N-H bonds of the nitrogen-rich cations. The structures of salts **78** and **86** were confirmed with single crystal X-ray diffraction.

In the ^{15}N NMR spectra of salts, three signals (~ -9.0, -9.5, and -44.0 ppm) are assigned to the TNP anion, the other signals are associated with the cations. HTNP, **82, 86**, and **87** taken as examples were measured in CD$_3$CN or DMSO [D6] solution with respect to CH$_3$NO$_2$ as external standard. Comparing the TNP anion with HTNP, the signals of pyrazole ring and nitro groups shift downfield with the difference of about 74 and 8 ppm. Comparison with TNP anion, the TNI anion has the similar chemical shift of nitro groups, and much lower chemical shift (about 69 ppm) of the ring nitrogen atoms. Interestingly, at 30 °C in (DMSO [D6]), there are only five signals (-8.9, -9.5, -43.0, -225.8, and -310.1 ppm) for **82**, but all signals (seven) are resolved at 80 °C.

The thermal stability of the TNP salts was determined by differential scanning calorimetric (DSC) measurements (Table 8). When the decomposition peak which appeared in the DSC was not sharp, the salts were examined using thermogravimetric analysis (TGA). While salts **74** and **81** decomposed without melting at 224 and 243 °C, respectively, the other salts have melting and decomposition temperatures ranging from 120 (**84**) to 206 °C (**82**) and 167 (**75** and **84**) to 243 °C (**81**). Densities for the TNP salts were measured with a gas pycnometer, and found in the range between 1.61 (**83**) and 1.77 gcm^{-3} (**77**). The triazolium salts exhibit a higher density than their guanidinium analogues, and 4-aminotriazolium TNP (**77**) has the highest density of 1.77 gcm^{-3}. Among the four guanidinium salts (**79, 80, 85, 86**), diaminoguanidinium TNP (**80**) has the lowest density at 1.62 gcm^{-3}. The two tetrazolium salts (**83** and **84**) have low densities of 1.61 and 1.64 gcm^{-3}, respectively. These relatively high densities are presumably caused by the high symmetry of the anion and the extensive intra- and intermolecular hydrogen bonds found in these salts. The oxygen balances (OB) of the TNP salts were calculated to fall between -50.6 (**83**) and -14.5 % (**74**).

The heats of formation (ΔH_f) of the cations and anion were calculated using the Gaussian 03 (Revision D. 01) suite of programs. The calculated ΔH_f of nitrogen-rich cations varies between 575.9 (guanidinium, **79**) and 1903.6 kJmol^{-1} (diguanidino-tetrazinium, **81**). Compared with 2,4,5-trinitroimidazolate anion (-148.5 kJmol^{-1}),[27a] the calculated ΔH_f of the TNP anion is less negative (-63.1 kJmol^{-1}). The heats of formation (ΔH_f) of the TNP salts are calculated using Born-Haber energy cycles. They are positive, and fall in the range 0.11 (**79**) to 1.45 kJg^{-1} (**84**).

With the data of density, heat of formation, and oxygen balance in hand, the detonation pressure (P) and velocity (vD), and specific impulse (I_{sp}) values of the TNP salts were calculated with Cheetah 5.0. Just as for **86** and **87**, the TNP salts have weaker detonation properties than the corresponding TNI salts arising mainly from lower densities.[27a] Based on the data in Table 8, the calculated detonation pressures and velocities lie in the range of 23.74 - 31.89 GPa and 7586 - 8543 ms^{-1}, which are superior to that of trinitrobenzene (TNT, 19.5GPa and 6881 ms^{-1}). Salt 77,

with detonation pressure and velocity at 31.89 GPa and 8543 ms^{-1}, is comparable with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, 31.15 GPa and 8114 ms^{-1}). The specific impulse values of the TNP salts ranging between 228.9 and 269.6 s suggest application of these energetic materials as propellants. Impact sensitivities of the TNP salts were measured by using a BAM Fallhammer apparatus with a 10 kg drop weight and found to be no less than 35 J placing them in the insensitive class.

It is interesting to compare the impact of salt formation on the properties of two insensitive explosives [HTNP (1.86 gcm^{-1}) and NTO (3-nitro-1,2,4-triazolate-5-one, 1.93 gcm^{-1})] such as density and heat of formation (and thus detonation properties). Salts **75**, **76**, and **77** have reduced densities from the parent to 1.69. 1.71, and 1.77 gcm^{-1} while the densities of the analogous NTO salts are also markedly reduced to 1.67, 1.71 and 1.68 gcm^{-1}, although it would appear that strong hydrogen bonding should contribute to enhancing the densities.[1f] While both parent explosives have slightly negative heats of formation (-0.07kJg^{-1} and -0.78 kJg^{-1},

Table 8. Properties of trinitropyrazolate salts compared with triaminoguanidium TNI (**85**), TNT, and TATB.*

Salt	$T_m{}^a$ °C	$T_d{}^b$ °C	P^c gcm^{-3}	$\Delta H_L{}^d$ kJmol^{-1}	$\Delta H_f{}^d$ (cation) kJmol^{-1}	$\Delta H_f{}^d$ (salt) kJmol^{-1}/kJg^{-1}	OB^e %	P^f Gpa	vD^g ms^{-1}	$I_{sp}{}^h$ s	IS^i J
74	-	224	1.73	502.7	626.4	60.5/0.28	-14.5	29.92	8461	263.0	40
75	158	167	1.69	473.1	835.0	299.0/1.10	-35.3	25.64	7871	245.0	>40
76	171	171	1.71	468.0	804.5	273.5/0.95	-36.2	26.00	7972	237.9	>40
77	168	168	1.77	471.9	936.3	401.2/1.40	-36.2	31.89	8543	269.6	>40
78	188	196	1.76	465.2	764.0	235.6/0.78	-37.1	27.67	8216	230.2	>40
79	163	235	1.66	476.5	575.9	28.3/0.11	-30.5	24.74	7865	235.6	>40
80	136	222	1.69	470.9	667.4	133.6/0.48	-31.8	26.85	8134	240.9	>40
81	-	243	1.68	1324.6	1903.6	452.3/0.75	-34.5	24.30	7817	228.9	>40
82	206	206	1.76	459.5	877.6	355.0/1.12	-37.8	28.83	8359	236.5	>40
83	166	219	1.61	449.6	887.7	375.0/1.19	-50.6	23.74	7586	230.5	>40
84	120	167	1.64	451.3	974.3	459.8/1.45	-37.8	25.20	7922	245.2	35
85	122	197	1.62	459.4	769.0	246.5/0.84	-32.9	25.34	7983	246.26	>40
86	125	184	1.65	455.9	871.5	352.7/1.15	-33.9	27.20	8236	250.5	>40
87	125	214	1.71	459.9	871.5	263.1/0.86	-33.9	28.89	8441	243.22	>40
TNT	80.4	295	1.65	-	-	-	-74.0	19.5	6881	-	15
TATB	-	318	1.94	-	-	-	-55.8	31.15	8114	-	50

*Syntheses of all compounds are given in Reference 45. ^{a} Melting temperature. ^{b} Decomposition temperature. ^{c} Density (25 °C). ^{d} Heat of formation. ^{e} Oxygen balance for $C_aH_bO_cN_d$, 1600(c-2a-b/2)/MW, MW = molecular weight of salt. ^{f} Detonation pressure. ^{g} Detonation velocity. ^{h} Specific impulse. ^{i} Impact sensitivity.

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respectively), the salts have increased positive values in the 0.95 to 1.40 kJg^{-1} and 1.70 to 2.33 kJg^{-1} ranges, respectively. However, while the salts have good thermal stabilities, none has detonation properties equivalent to the parent.

Crystals of both **78** and **86**, suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of aqueous solutions at room temperature. Their structures are shown in Figures 8 and 9. Both of them crystallize in the triclinic *P*-1 space group with one cation per TNP anion. The transfer of each proton from the NH group of HTNP to the ring nitrogen of 3,4-diaminotriazole and triaminoguanidine is confirmed in Figures 8a and 9a. For **78**, the

8a   **8b**
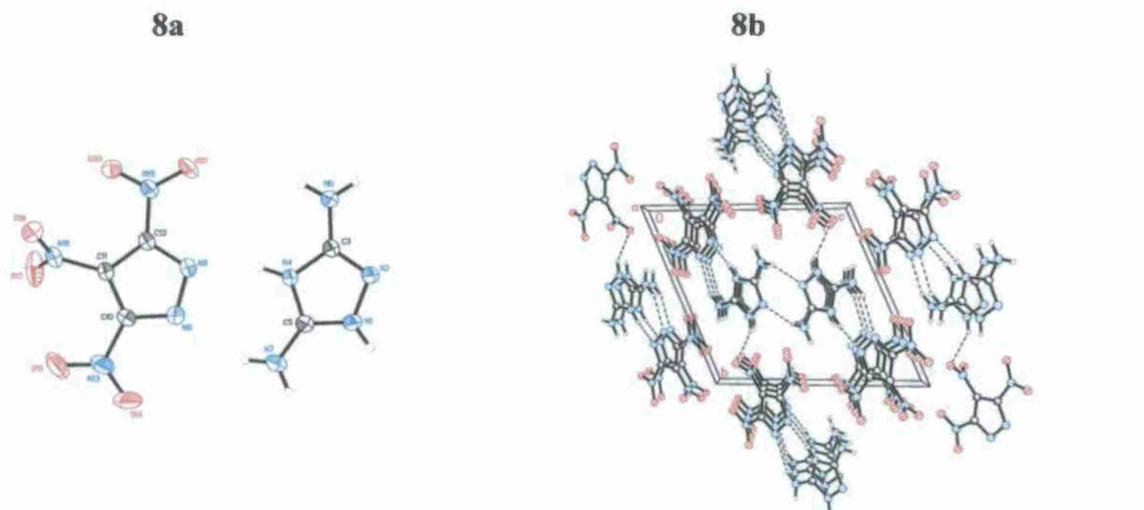
Figure 8. (a) Thermal ellipsoid plot (30%) and labeling scheme for 3,5-dinitrotriazolium TNP (**78**). Hydrogen atoms included but are unlabelled for clarity. (b) Ball and stick packing diagram of **78** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

9a   **9b**
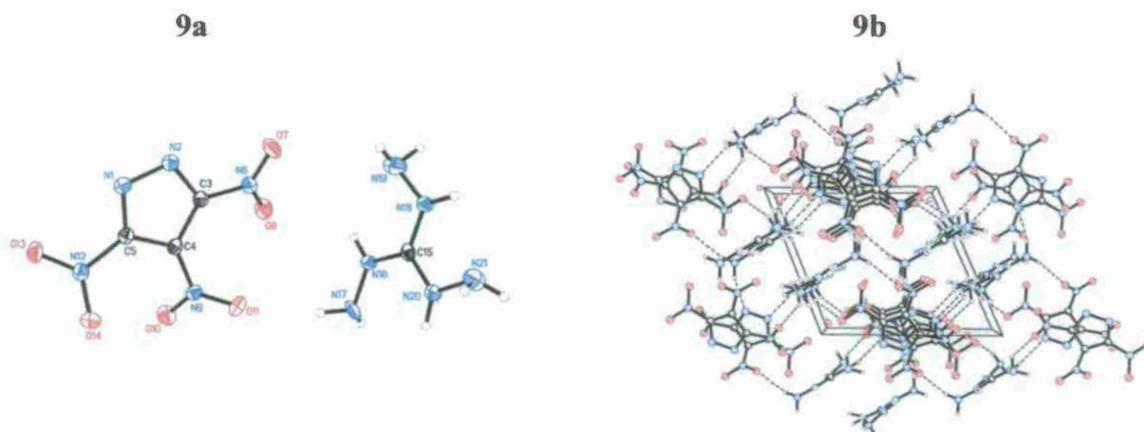
Figure 9. (a) Thermal ellipsoid plot (30%) and labeling scheme for trinitroguanidium TNP (**86**). Hydrogen atoms included but are unlabelled for clarity. (b) Ball and stick packing diagram of **86** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

pyrazole and the triazole rings are in the same plane. In the TNP anion, 3(5)-nitro groups are in the plane of the pyrazole ring, and 4-nitro group is twisted out of the plane of the pyrazole ring (116.2°). The extensive hydrogen bonding interactions between cations and anions form a complex 3D network.

In summary, a family of energetic salts based on nitrogen-rich cations and the 3,4,5-trinitropyrazolate anion (TNP) was prepared and fully characterized. The structures of 3,5-diaminotriazolium (**78**) and triaminoguanidinium (**86**) TNP were confirmed by single crystal X-ray diffraction showing that there are extensive hydrogen bonding interactions between the cation and anion in these salts. Densities for the TNP salts, measured with a gas pycnometer, were found to fall in the range between 1.61 (**83**) and 1.77 gcm^{-3} (**77**) placing them in a class of relatively dense compounds. By using Cheetah 5, their detonation pressures and velocities were calculated to fall in the range of $23.74 - 31.9$ GPa and $7586 - 8543$ ms^{-1}. Salt **77**, with detonation pressure and velocity at 31.89 GPa and 8543 ms^{-1}, is comparable with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, 31.15 GPa and 8114 ms^{-1}). The specific impulse values of the TNP salts range between 228.9 and 269.6 s. Except for **74** (40 J) and **84** (35 J), the impact sensitivities of the TNP salts are more than 40 J. Based on rather high detonation properties, low impact sensitivity, and high stability, the TNP salts have potential as energetic materials.

I. Synthesis and properties of 3,4,5-trinitroyrazole-1-ol and its energetic salts.

Hydroxyl derivatives of fully C-nitrated azoles (nitroazoles-ol) with positive oxygen balance (based on CO_2) have become interesting, among which 5-nitrotetrazole-2-ol shows better detonation performance than 5-nitrotetrazole.[46] Based on our calculations, 2,4,5-trinitroimidazole-ol (HTNIO) and 3,4,5-trinitropyrazole-ol (HTNPO) are also more powerful than their corresponding parents, which exhibit the potential as good energetic materials. In this work, preparation of 3,4,5-trinitropyrazole-ol and 2,4,5-trinitroimidazole-ol was attempted by using oxone as an oxidizing agent.[46,47] Furthermore, 3,4,5-trinitropyrazole-ol was stabilized by forming nitrogen-rich salts.

Ammonium 2,4,5-trinitroimidazole (NH_4TNI) and ammonium 3,4,5-trinitropyrazole (NH_4TNP) were prepared based on literature methods.[26g,45] Attempts were made to oxidize NH_4TNI and NH_4TNP with oxone at 55 °C in an effort to prepare the corresponding trinitroazole-ol.[46,47] It was found that NH_4TNI could not be oxidized further (Scheme 20). However, NH_4TNP (**88**) was successfully oxidized to ammonium 3,4,5-trinitropyrazole-1-olate (**89**, NH_4TNPO) which was confirmed with NMR and IR spectra, and elemental analysis. The failure to oxidize NH_4TNI may result from steric hindrance arising from the presence of the nitro groups bonded to the carbon atoms vicinal to the nitrogen atom in the TNI ring.
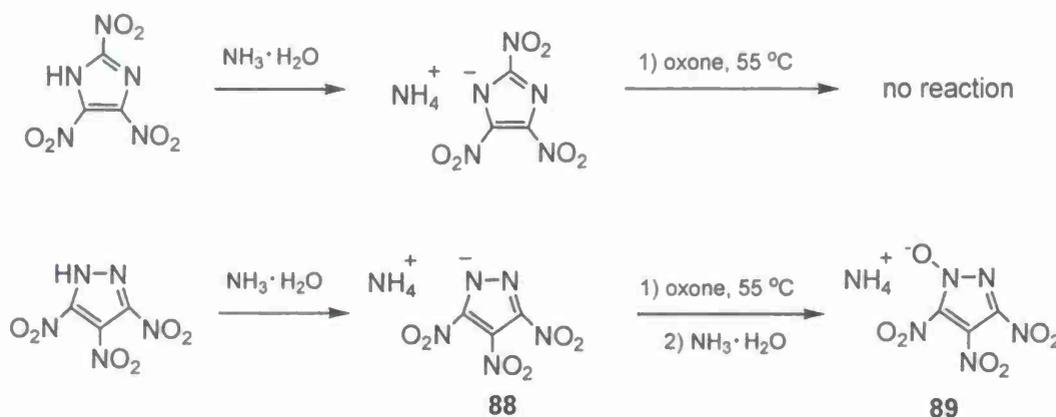
Scheme 20. Synthesis of ammonium trinitroimidazole-1-olate and trinitropyrazole-1-olate salts.

3,4,5-Trinitropyrazole-1-ol (HTNPO, **90**) was obtained as an yellow oil in high yield (95%) from the acidification of **89** with H_2SO_4 (Scheme 21), and confirmed with NMR (^1H, ^{13}C, and ^{15}N) and IR spectra. Compared with 3,4,5-trinitropyrazole (OC, 47.27%; OB, 19.70%), **90**

possesses higher oxygen content and has a positive oxygen balance (OC, 51.13%; OB, 25.56%). While **90** is thermally stable with the onset decomposition point at 146 °C, it is very sensitive to impact with the value of 1 J. Surprisingly, **90** can not be solidified even upon standing for several weeks. Many attempts to solidify or recrystallize **90** from solvents including benzene, ethyl acetate, hexane, etc. failed. With such a high sensitivity, it is difficult to suggest applications for **90**. Based on the fact that energetic salts usually possess lower sensitivity, higher thermal stability, and lower vapor pressure than their neutral precursors, a series of 3,4,5-trinitropyrazole-1-olate salts was prepared in high yield by neutralizing guanidine carbonate, triazole, 3-aminotriazole, 4-aminotriazole, 3,5-diaminotriazole, and 3,4,5-triaminotriazole with HTNPO, respectively (Scheme 21). These salts were also confirmed with NMR and IR spectra, and elemental analysis.
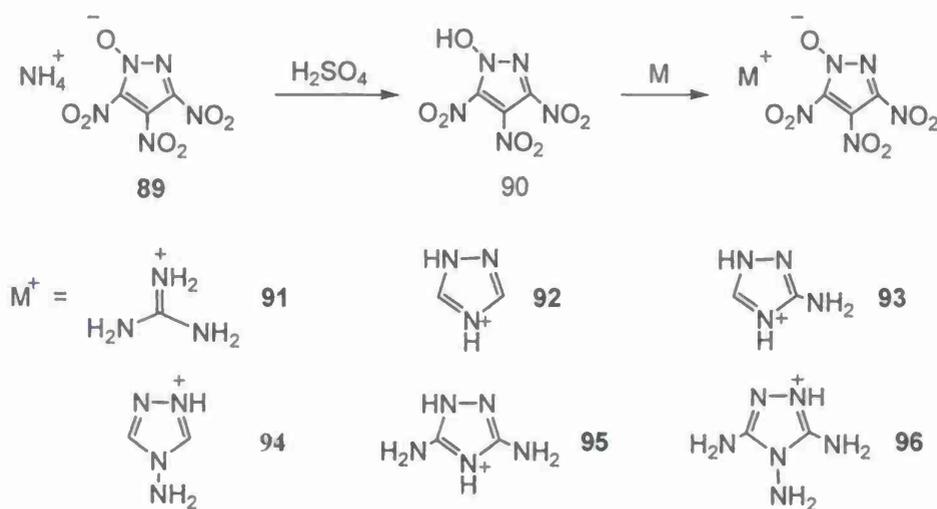
Scheme 21. Synthesis of 3,4,5-trinitropyrazole-1-ol and its salts.

In ^{1}H NMR spectra, the hydrogen signals were easily assigned, since there is only one proton associated with HTNPO, and no proton with the TNPO anion. In ^{13}C NMR spectra, there are three very weak signals ($\delta = \approx 131$, 130, and 119 ppm) assigned to the HTNPO or TNPO anion, the other signals are associated with the cations. In the ^{15}N NMR spectra, HTNPO, **89**, **91**, and **96** are taken as examples and measured in [D6]DMSO with respect to CH_3NO_2 as external standard. Five signals ($\delta = \approx -27$, -28, -31, -92, and -95 ppm) are assigned to HTNPO because of its unsymmetrical structure. The signals of the TNPO anion are very similar to those of HTNPO, except for ~3 ppm lower chemical shift of the N-O$^-$ signal. For **89**, the signal of NH_4^+ is not shown in ^{15}N NMR spectra. However it is clearly shown in ^{14}N NMR spectra with the chemical shift at -358 ppm.

The thermal stabilities of the 3,4,5-trinitropyrazole-1-olate salts were determined by differential scanning calorimetric (DSC) measurements (Table 9). All the salts decomposed without melting, ranging from 118 (**7**) to 186 °C (**95**). Densities were measured with a gas pycnometer, and found in the range between 1.72 (**91**) to 1.82 gcm^{-3} (**89**). The relatively high densities are presumably caused by the extensive hydrogen bonding found in these salts. The values for the heats of formation of the cations are from the literature.[45] The heat of formation of the anion (-91.21 kJmol^{-1}) was calculated by the Gaussian 03 (Revision D. 01) suite of programs. The positive heats of formation of the TNPO salts were calculated by using Born-Haber energy cycles and were found in the range 0.01 (**91**) to 1.26 kJg^{-1} (**94**). The detonation pressures and velocities were calculated with EXPLO5.[13] Of the above salts, **89** shows the highest detonation pressure (35.1 GPa) and velocity (8676 ms^{-1}), which are very close to RDX (35.2 GPa; 8977 ms$^-$

'). Impact sensitivities of these salts were measured by using a BAM Fallhammer apparatus with a 10 kg drop weight and found to exceed 40 J, except **89** (6 J).

It is interesting to compare 3,4,5-trinitropyrazole-1-ol and its salts with the corresponding 3,4,5-trinitropyrazole and its salts, which shows the effects of the HO-N group on the properties of the resulting compounds. With the slightly lower heats of formation (TNPO/TNP, 118.5/133.6 kJmol^{-1}; TNPO anion/TNP anion, -91.21/-63.1 kJmol^{-1}), the TNPO compounds show many other promising properties. Taking the ammonium salt as an example (Table 9), the TNPO salt

Table 9. Properties of 3,4,5-trinitropyrazole-1-olate salts compared with TNT and RDX.*

Salt	t_m °C	t_d °C	ρ gcm^{-3}	ΔH_f(cation) kJmol^{-1}	ΔH_L kJmol^{-1}	ΔH_f(salt) kJmol^{-1}/kJg^{-1}	OC%/OB %	P Gpa	VD ms^{-1}	IS J
88[l]	-	224	1.73	626.4	502.7	60.5/0.28	43.62/7.27	29.92	8461	40
89	-	176	1.82	626.4	500.1	35.1/0.15	47.44/13.55	35.07	8676	6
90	-	146	1.90			118.5/0.54	51.13/25.56	36.40	8669	1
91	-	171	1.72	566.7	472.4	3.09/0.01	40.27/0.00	28.77	8176	>40
92	-	140	1.73	835.0	468.8	274.9/0.95	38.87/0.00	29.50	8175	>40
93	-	132	1.73	804.5	462.8	250.5/0.83	36.95/-2.64	29.16	8177	>40
94	-	118	1.74	936.3	463.5	381.6/1.26	36.95/-2.64	30.82	8345	>40
95		186	1.76	764.0	459.1	213.7/0.67	35.20/-5.03	29.74	8261	>40
96	-	185	1.77	877.6	454.5	331.9/1.00	33.62/-7.20	31.14	8442	>40
TNT	80.4	295	1.65			-67.0/-0.30	42.27/-24.66	19.5	6881	15
RDX	-	230	1.82			92.6/0.42	43.22/0.00	35.17	8977	7.4

*Syntheses of all compounds are given in Reference 48. [a] Melting temperature. [b] Decomposition temperature. [c] Density (25 °C) [d] Calculated heat of formation of cation. [e] Calculated lattice energy of salt. [f] Calculated heat of formation of salt. [g] Oxygen content. [h] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, 1600(c-a-b/2)/MW, MW = molecular weight of salt. [i] Detonation pressure. [j] Detonation velocity. [k] Impact sensitivity. [l] Reference 45.

possesses some better properties than the corresponding TNP salt, including density (1.82/1.73 gcm^{-3}), oxygen content (47.44%/43.62%) and balance (13.55/7.27%), detonation pressure (35.07/29.92 GPa) and velocity (8676/8461 ms^{-1}). Unfortunately, the thermal stability (176/224 °C) and impact sensitivity (6/40J) of the TNPO salt are not as competitive as those of its corresponding TNP salt.

In order to understand the structure of the 3,4,5-trinitropyrazole-1-olate anion compared to the 3,4,5-trinitropyrazolate anion, **88** and **89** were recrystallized from ethyl acetate, and characterized by single-crystal X-ray diffraction (Figure 10). The crystallographic data are summarized in Table 2. Compound **88** crystallizes in the monoclinic P2$_1$/n space group with one ammonium cation per trinitropyrazolate anion. Compound **89** crystallizes in the triclinic P-1 space group with one ammonium cation per trinitropyrazole-1-olate anion, with one ethyl acetate molecule of solvation. The transfer of each proton from the NH group of HTNP or OH group of HTNPO to ammonia is confirmed by the structures in Figure 10.

**10a**   **10b**
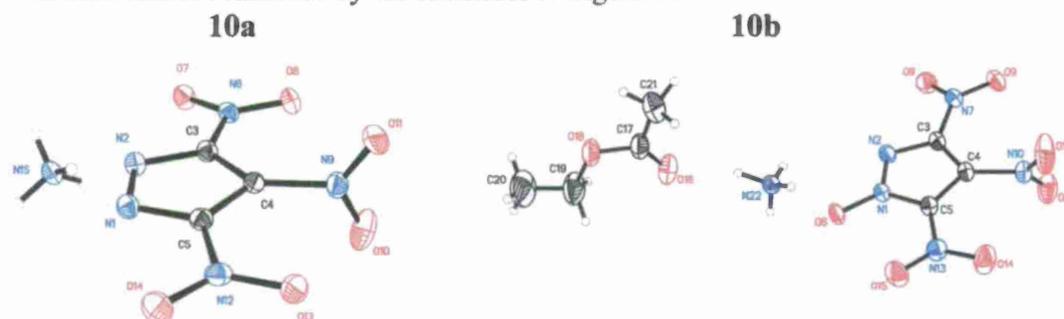
Figure 10. 10a) Thermal ellipsoid plot (50%) and labeling scheme for ammonium 3,4,5-trinitropyrazolate (**88**). 10b) Thermal ellipsoid plot (50%) and labelling scheme for ammonium 3,4,5-trinitropyrazole-1-olate (**89**). Hydrogen atoms included but are unlabeled for clarity.

Furthermore, the structure of triazolium 3,4,5-trinitropyrazole-1-olate (**92**) was confirmed by single-crystal X-ray diffraction (Figure 11). Compound **92** crystallizes in the orthorhombic $P2_12_12_1$ space group with one triazolium cation per TNPO anion. The transfer of each proton from the NH group of HTNP to triazole is confirmed in Figure 11a. Its packing structure is configured by hydrogen bonds (N(17)-H(17)...O(6)#1; N(19)-H(19)...O(6)#2). The extensive hydrogen-bonding interactions between cations and anions form a complex 3D network (Figure 11b).

11a 11b
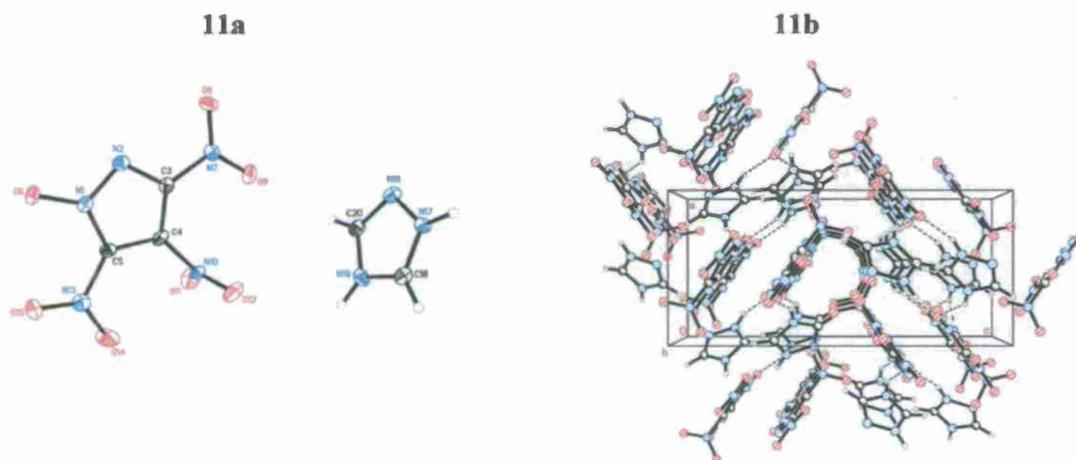
Figure 11. 11a) Thermal ellipsoid plot (50%) and labeling scheme for triazolium 3,4,5-trinitropyrazole-1-olate (**92**). Hydrogen atoms included but are unlabled for clarity. 11b) Ball and stick packing diagram of **92** viewed down the b axis. Dashed lines indicate strong hydrogen bonding.

In summary, 3,4,5-trinitropyrazole-1-ol and its salts were prepared and fully characterized by using NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis for **88, 89,** and **92**. 3,4,5-Trinitropyrazole-1-ol with its high oxygen content (51.13%) could be the green replacement of the currently used oxidizer (NH_4ClO_4). However, the high impact sensitivity (1 J) restricts its application. The resulting nitrogen-rich salts with acceptable impact sensitivities (6-40 J) and detonation performance (*P*, 28.77-35.07 Gpa; *vD*, 8175-8676 ms^{-1}) have the potential to be useful energetic materials.

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18. Alternate methods employing 70% HNO_3 were used for the synthesis of nitroiminotetrazoles **43** and **44**. After 3 days stirring the reaction mixture was dried under air. The white solid product was recrystalized from water. However, the yield was 30−34%.

19. At 0°C, 2 mmole 1-substituted aminotetrazole was added in small portions to 10 mL 100% HNO_3. The reaction mixture was stirred at ambient temperature for 18 hours. The solution was poured into 20 g ice. After stirring for 3 hours, the product was precipitated, filtered, washed with water, and dried in air at room temperature.

20. Crystallographic data for **40**: $C_3H_6N_6O_3$: $M_r = 174.14$; crystal size = 0.88 x 0.48 x 0.34 mm^3; triclinic, *P*-1, a = 7.1095(13) Å, b= 7.1116(13) Å, c = 7.8928(15) Å, $\alpha = 89.235(2)°$, $\beta = 66.303(2)°$, $\gamma = 66.804(2)°$, $V = 330.86(11)$ Å^3, $Z = 2$, $2\theta_{max} = 56.6°$, $\rho_{calc} = 1.748$ Mg/m^3, $\mu = 0.153$ mm^{-1}, $F(000) = 180$, $R_1 = 0.0393$ for 1475 observed ($I > 2\sigma I$) reflections and 0.0419 for all 1616 reflections, goodness-of-fit = 1.065, 110 parameters. **43**: $C_4H_6N_{12}O_4$: $M_r = 286.21$; crystal size = 0.25 x 0.12 x 0.11 mm^3; monoclinic, $P2_1$/n, $a = 8.182(3)$ Å, $b = 6.614(2)$ Å, $c = 10.463(3)$ Å, $\alpha = 90°$, $\beta = 112.380(4)°$, $\gamma = 90°$, $V = 523.6(3)$ Å^3, $Z = 2$, $2\theta_{max} = 56.6°$, $\rho_{calc} = 1.815$ Mg/m^3, $\mu = 0.159$ mm^{-1}, $F(000) = 292$, $R_1 = 0.0808$ for 1124 observed ($I > 2\sigma I$) reflections and 0.0868 for all 1265 reflections, goodness-of-fit = 1.228, 91 parameters.

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APPENDIX - New molecular species and salts with attractive properties.

Molecular species	d g/cm³	T_d °C	ΔH_f kJ/g	P Gpa	D m/s	IS J	OP %
4	1.78	183	-0.19	31.6	8657	6	41
5	1.75	183	1.45	35.6	8933	20	43
14	1.66	116	3.15	31.5	8660	5	30
19	1.90	157	3.58	46.7	9867	1	28
25	1.81	134	3.47	38.4	9200	1.5	30
41	1.71	117	1.60	30.9	8496	>40	37
43	1.86	194	3.63	38.2	9329	10	22
46	1.76	139	2.55	33.0	8741	3	31
51	1.94	135	0.46	35.5	8943	9	49
53	1.91	87	0.38	38.4	9229	9.5	44
54	1.88	153	0.34	36.9	9006	13	46
56	1.83	150	1.20	36.7	8964	1.5	42
57	1.78	165	1.03	33.8	8742	5.5	39
59	1.78	125	0.54	33.8	8803	6	39
90	1.90	146	0.54	36.4	8669	1	51
SALTS							
16	1.63	156	2.98	32.3	9036	4	25
20	1.71	167	2.38	33.0	8984	1.5	30
26	1.72	202	2.24	33.3	9014	2	27
27	1.73	169	2.92	35.5	9305	1.5	25
33	1.70	130	2.78	32.2	8789	6	27
34	1.78	147	2.76	33.3	9030	2	21
60	1.67	139	2.82	37.8	9482	11	31
61	1.92	182	2.18	37.3	8973	10	33
72	1.94	113	1.90	36.2	8997	14.5	22
89	1.82	176	0.15	35.1	8676	6	47

Common explosives/oxidizers

ADN	1.81	145		31.0	8681		
TNT	1.65	295	0.30	19.5	6881	15	42
RDX	1.82	230	0.42	35.2	8977	7.4	43
HMX	1.91	287	0.35	39.6	9320	7.4	43
PETN	1.78	160	-1.59	31.4	8564	2.9	61
TATB	1.94	350(T_m)	-0.60	31.2	8114	50	37
AP	1.95						54

Conclusions

More than 61 papers that acknowledge ONR's support of our work have appeared in the world's best chemical journals during the period covered by this report, 2009-2012. A particularly useful review appeared in *Chemical Reviews* in 2011 (publication 45).

1) Our empirical method for estimation of densities of salts and molecular species is rapid and gives values that agree remarkably well with those measured experimentally or calculated from X-ray data. The publication which describes this straightforward methodology is currently one of our most cited.

2) Of the very large number of energetic salts synthesized that are comprised of one of eight different nitro-containing anions, including 5-nitroiminotetrazolates, mono-oxy-nitroimino-tetrazolates and bis-oxy-nitroiminotetrazolates; 1-hydrazinyl-2,2-dinitro-ethanamine salts; 5-nitro-3-trinitromethyl-1H-1,2,4-triazolates, and 5,5'-bis(trinitromethyl)-3,3'-azo-1H-1,2,4-triazolates; 3,4,5-trinitropyrazolate; and trinitropyrazole-1-olate salts, there are five salts that exhibit detonation pressures and velocities that are competitive with or superior to RDX; none superior to HMX. Of these, only three have lower impact sensitivities. The salts are dihydrazinium bis-oxy-nitroiminotetrazolate (**27**), hydrazinium 1-hydrazinyl-2,2-dinitro-ethanamine (**60**), potassium 1-hydrazinyl-2,2-dintroethanamine (**61**), bis(guanidinium)tetrazinium 5,5'-bis(trinitromethyl)-3,3'-azo-1H-1,2,4-triazolate (**72**), and ammonium 3,4,5-trinitropyrazole-1-olate (**89**) (See Appendix).

3) Not surprisingly, a larger fraction of the molecular compounds outperform RDX and HMX with respect to detonation properties and impact sensitivities than is the case for salts. In general, the densities are $1.75 - 1.94$ g/cm^3, higher on average than those for the energetic salts, which are effective in enhancing detonation properties. There are nine molecular species prepared during this work that have superior detonation properties. Eight are superior to RDX, i. e., N1, N2, N3-trinitro-1,2,3-propanetriamine (**5**), 1,1'-[methylenebis(oxy)]bis[1,2-dihydro-N-nitro]5H-tetrazol-5-imine (**19**), 1,2-[ethylenebis(oxy)]bis[1,2-dihydro-N-nitro]5H-tetrazol-5-imine (**25**) bis(5-nitroiminotetrazole)ethane (**43**), 5-nitro-3-trinitromethyl-1H-[1,2,4]triazole (**51**), 3-dinitromethyl-5-nitro-1H-[1,2,3]triazole hemihydrate (**53**), 1-methyl-5-nitro-3-trinitromethyl-1H-[1,2,4]triazole (**54**), 5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole hemihydrate (**56**) and 3,4,5-trinitropyrazole-1-ol (**90**). One exhibits higher detonation values than HMX, i. e., 1,1'-[methylenebis(oxy)]-bis[1,2-dihydro-N-nitro]5H-tetrazol-5-imine (**19**). With the exception of **19, 25, 56,** and **90,** all are moderately less impact sensitive than RDX or HMX. (See Appendix).

4) Oxygen content is the important attribute in the development of materials to replace the environmentally unfriendly ammonium perchlorate as an oxidizer. Only one salt, ammonium 3,4,5-trinitropyrazole-1-olate (**89**), whose detonation properties approach those of RDX has oxygen content essentially equivalent to or superior to RDX (HMX).

5) A larger number of the molecular species have encouraging oxygen percentages equivalent to or better than RDX (HMX) with concomitant good detonation values, i. e., pentaerythrityl tetranitramine (**4**), **5, 51, 53, 54, 56,** 1,1'-dimethyl-5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole (**II-57**), 1-amino-1-hydrazino-2,2-dinitroethene (**II-59**) and **90.** Compounds **5, 43, 51, 53,** and **54** are less sensitive to impact than RDX (HMX).

6) In a very large number of the syntheses examined, water is the solvent of choice which speaks positively to hydrolytic stability of the compounds and enhances the greenness of the synthesis.

7) The value of salts is hindered by the inability to introduce cations, unless metals or simple ammonium or hydrazinium, that will contribute positively to the desired properties. One positive point is that it is possible to enhance the hydrogen bonding capability thus increasing the density.

8) In general, thermal stabilities are somewhat < 200 °C; less than that of RDX or HMX.

9) The design and characterization of molecular species will more likely lead to energetic materials with the desired properties.

10) Several of the new materials (**51, 53, 54, 57, 72**) may be worthy of transitioning to 6.2 or being an important component of insensitive high explosive formulations.

11). The knowledge gained from this work will provide a remarkably strong foundation on which to build future efforts in designing suitable replacements for ammonium perchlorate and upgrading the performance of new molecular species to meet the RDX/HMX/TATB goal.

Awards

1. Professor Shreeve was named an inaugural University of Idaho Distinguished Professor (2011).

2. Professor Shreeve was selected as an American Chemical Society Fellow (2010).

3. The Idaho NSF EPSCoR state committee has established the "Jean'ne M. Shreeve NSF EPSCoR Research Excellence Award" to honor outstanding Idaho EPSCoR scientists in recognition of her leadership during 22 years of service to Idaho's EPSCoR program (2011).

4. Cited as one of the top 20 papers in *Chemistry of Materials* in 2009 - Xue, H.; Gao, H.; Twamley, B.; Shreeve, J. M. "Energetic Salts of 3-Nitro-1,2,4-triazole-5-one (NTO), 5-Nitroaminotetrazole and Other Nitro-substituted Azoles," *Chemistry of Materials*, **2007**, *19*, 1731-1739.

5. "The most important reactions in organic and organometallic chemistry" in ~200/502 of our published papers cited by *ChemInform*.

6. Featured in C&E News – Central Science – 11-3-2011 - Thottempudi, V.; Shreeve, J. M. "Synthesis and Promising Properties of a New Family of High-Density Energetic Salts of 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole and 5,5'-bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole," *Journal of the American Chemical Society*, **2011**, *133*, 19982-19992.

7. Cited in ACS Noteworthy Chemistry – 05-28-2012 - Gao, H.; Shreeve, J. M. "Ionic Liquid Solubilized Boranes as Hypergolic Fluids," *Journal of Materials Chemistry*, **2012**, *22*, 11022-11024.

8. One of top-10 most read *Journal of Materials Chemistry* articles in January 2011. Hot article - Garg. S.; Shreeve, J. M. "Trifluoromethyl- or pentafluorosulfanyl-substituted poly-1,2,3-triazole compounds as dense stable energetic materials," *Journal of Materials Chemistry*, **2011**, *21*, 4787-4795.

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